Knowledge Exchange –
Source Removal Technologies

Presentation Overview

- Introduction: Science vs. Technology
- Plume Treatment
- NAPL Source Zone Treatment
- The DNAPL Problem
- Summary and Conclusions

Problem Statement: Technology vs. Science

- Greeks considered them to be two different things:
  - Science was for the “thinker”
  - Technology was for the “common man”
- Throughout most of history, technology has had little to do with science.
- Technology approach comes from intuitive thought and then develops from failures.

Or put another way:

**In Theory,
Practice and Theory
Should Be in Good Agreement.**

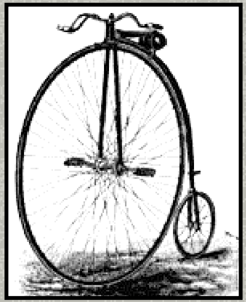
**In Actual Practice,
Theory and Practice
Rarely Agree.**

Case Study: Development of the Bicycle

- Technology Development without Science

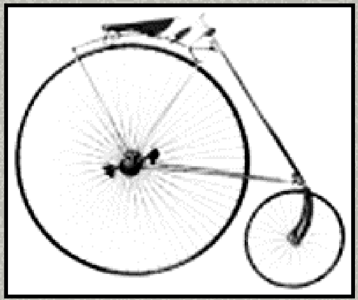
The Walking Machine
1817

The "Boneshaker"
1865

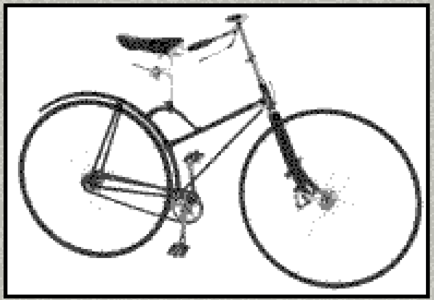


The High-Wheel Bicycle
1870

"Taking a Header"



The High-Wheel Safety



The Hard-Tired Safety

The Pneumatic-Tired Safety
1878

The Kids' Bike

Case Study: Development of the Bicycle

- Technology Development without Science

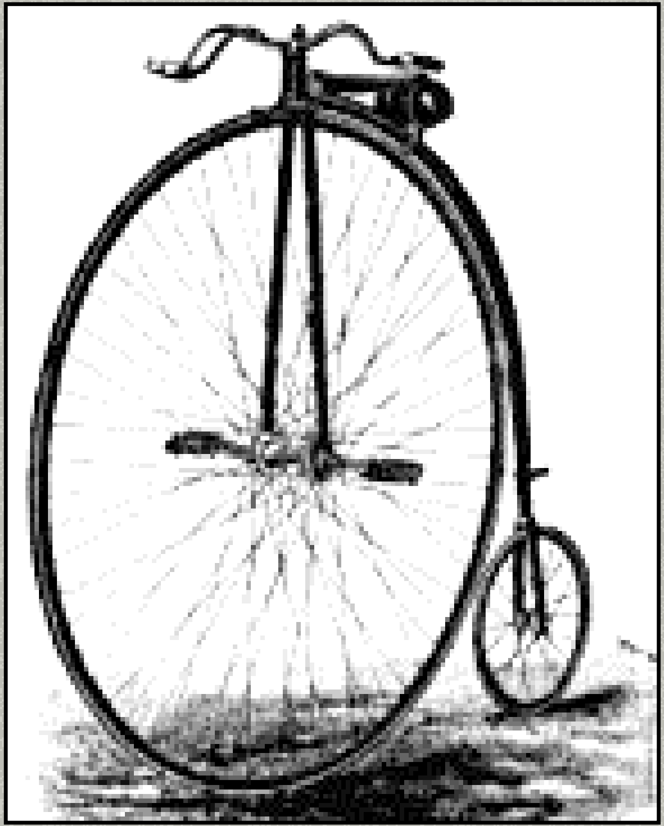
The Walking Machine – 1817

Case Study: Development of the Bicycle (cont.)

The “Boneshaker” – 1865

Case Study: Development of the Bicycle (cont.)

The High-Wheel Bicycle – 1870

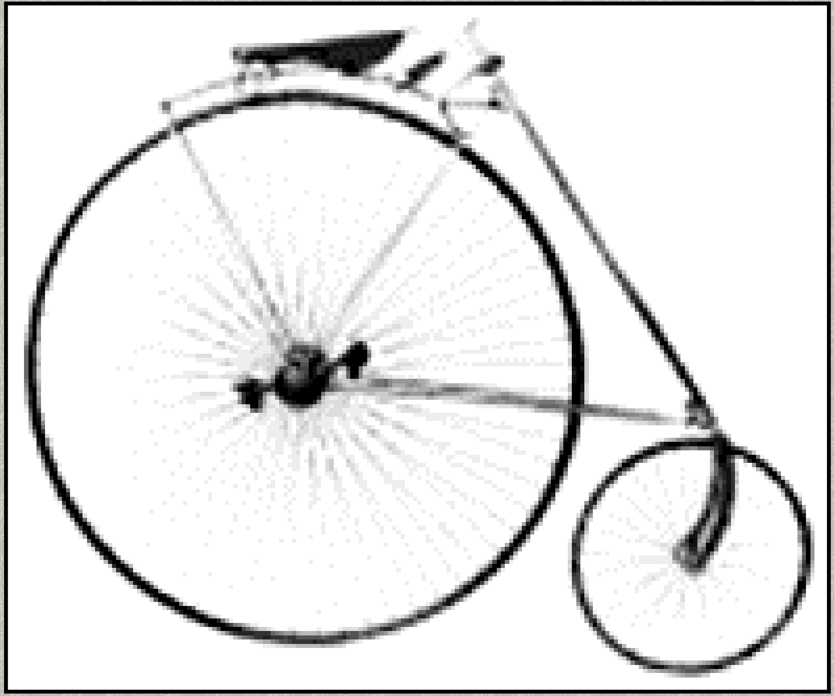


Case Study: Development of the Bicycle (cont.)

"Taking a Header"

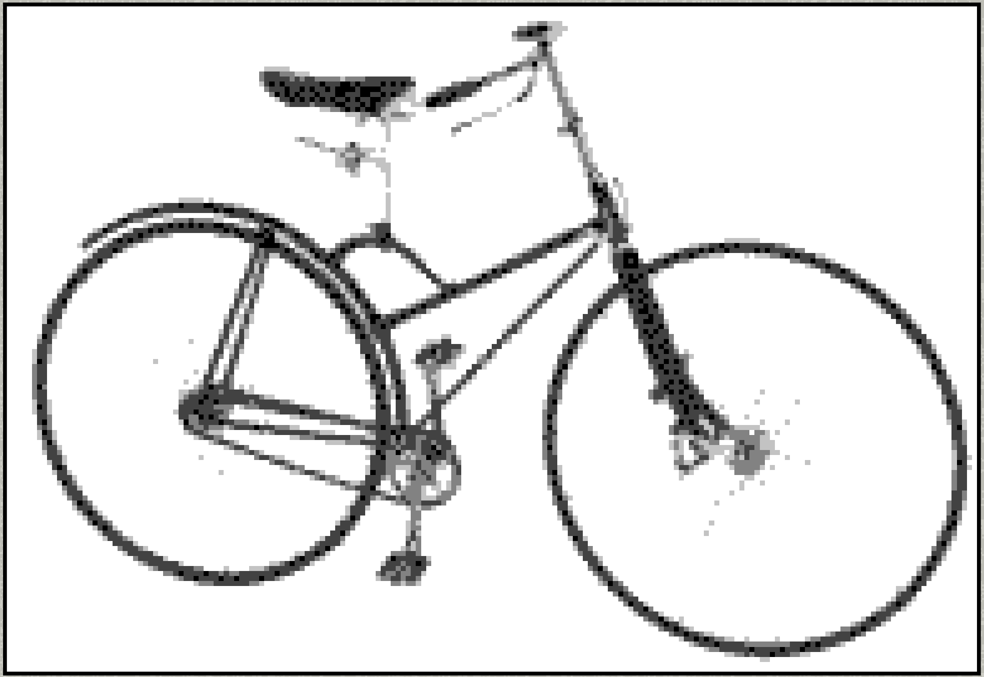
Case Study: Development of the Bicycle (cont.)

The High-Wheel Safety



Case Study: Development of the Bicycle (cont.)

The Hard-Tired Safety



Case Study: Development of the Bicycle (cont.)

The Pneumatic-Tired Safety – 1878

Case Study: Development of the Bicycle (cont.)

The Kids' Bike

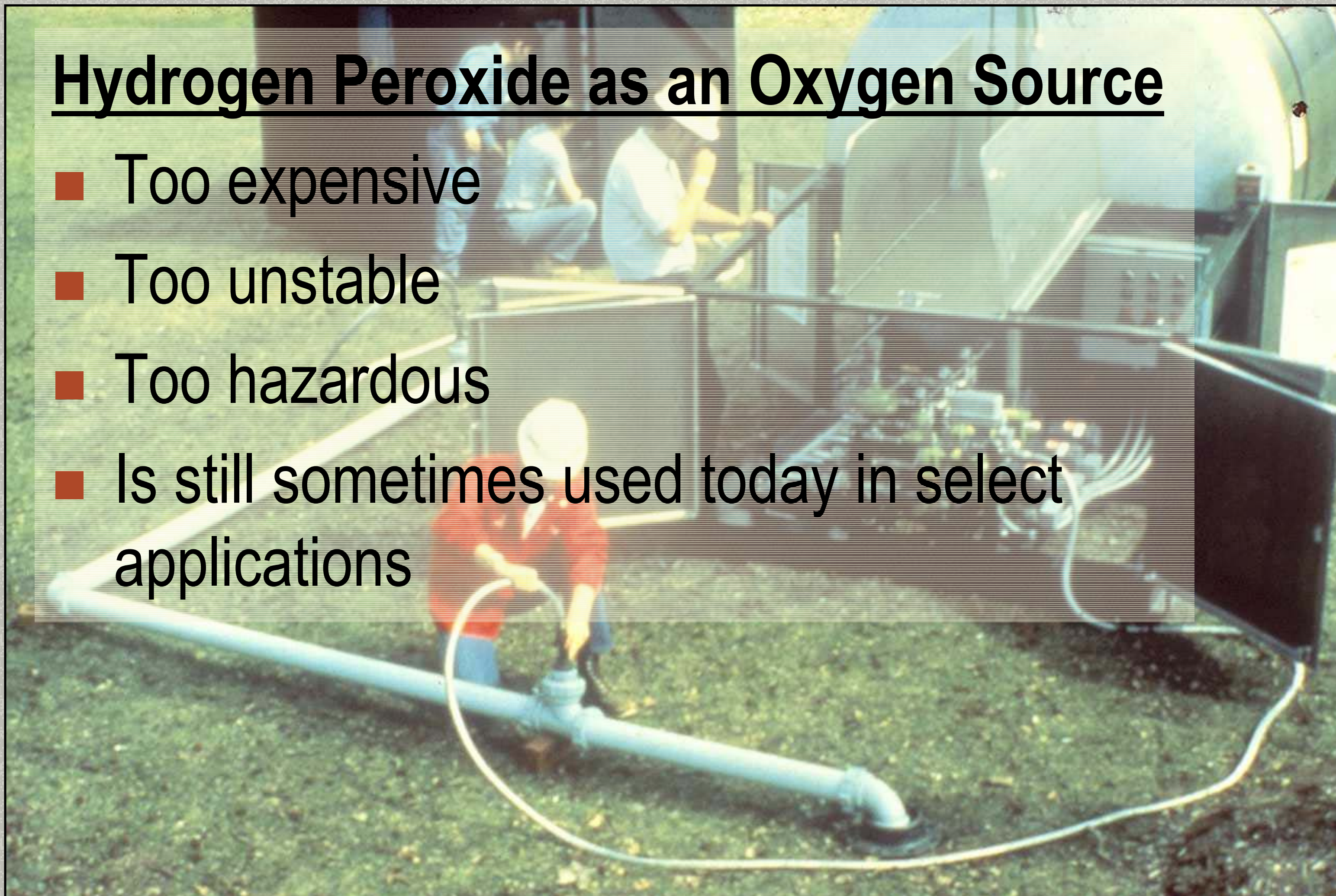
Case Study: Development of the Bicycle (cont.)

Modern Mountain Bike

Science to Technology Model

- More recently, technology is viewed as the application of science.
- Werner Heisenberg: “Science clears the fields upon which technology can build.”
- Examples of Science-Lead Technologies:
  - Atomic weapons
  - Space program
  - Computers

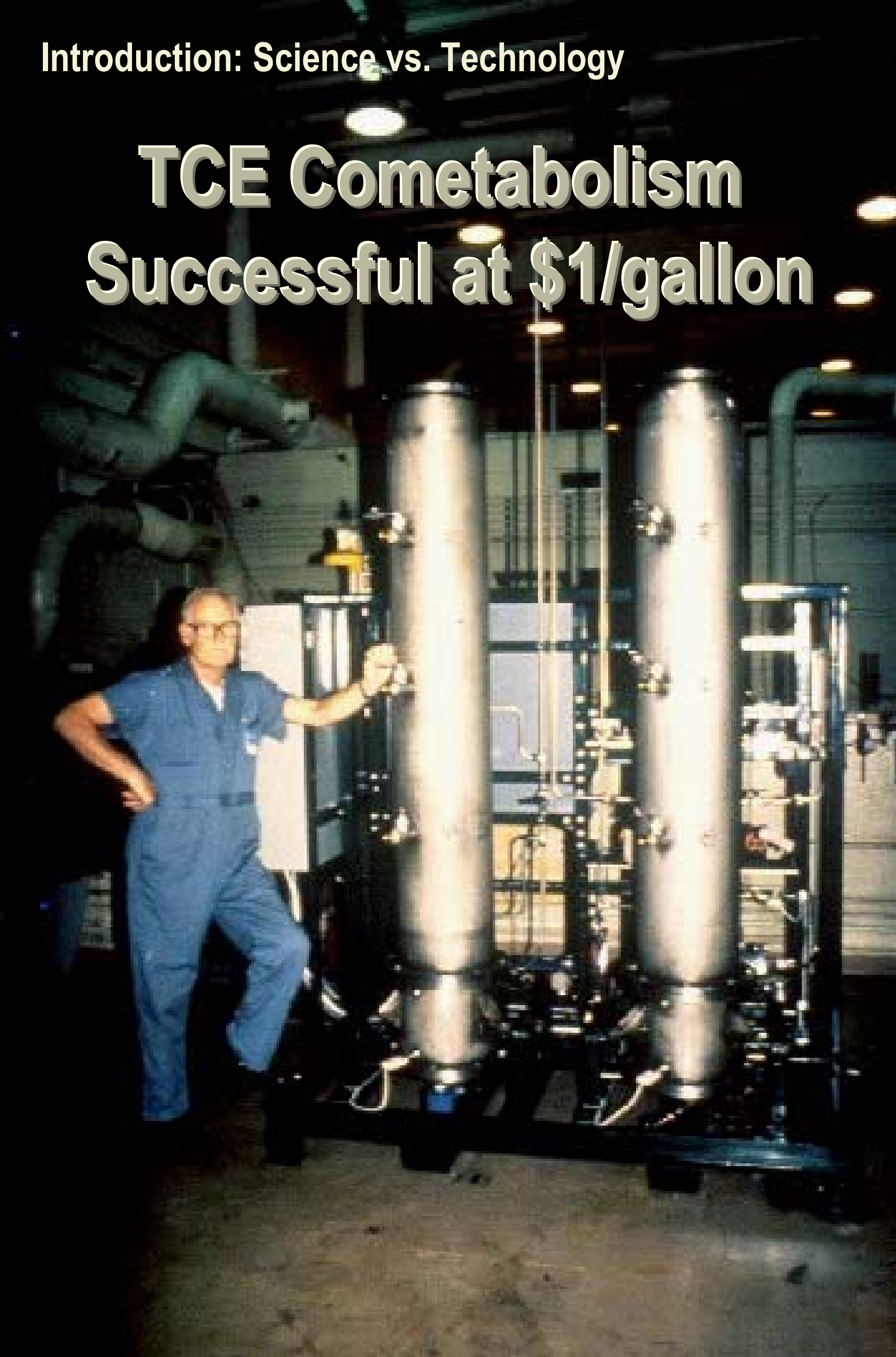
Hydrogen Peroxide Injection – 1980s

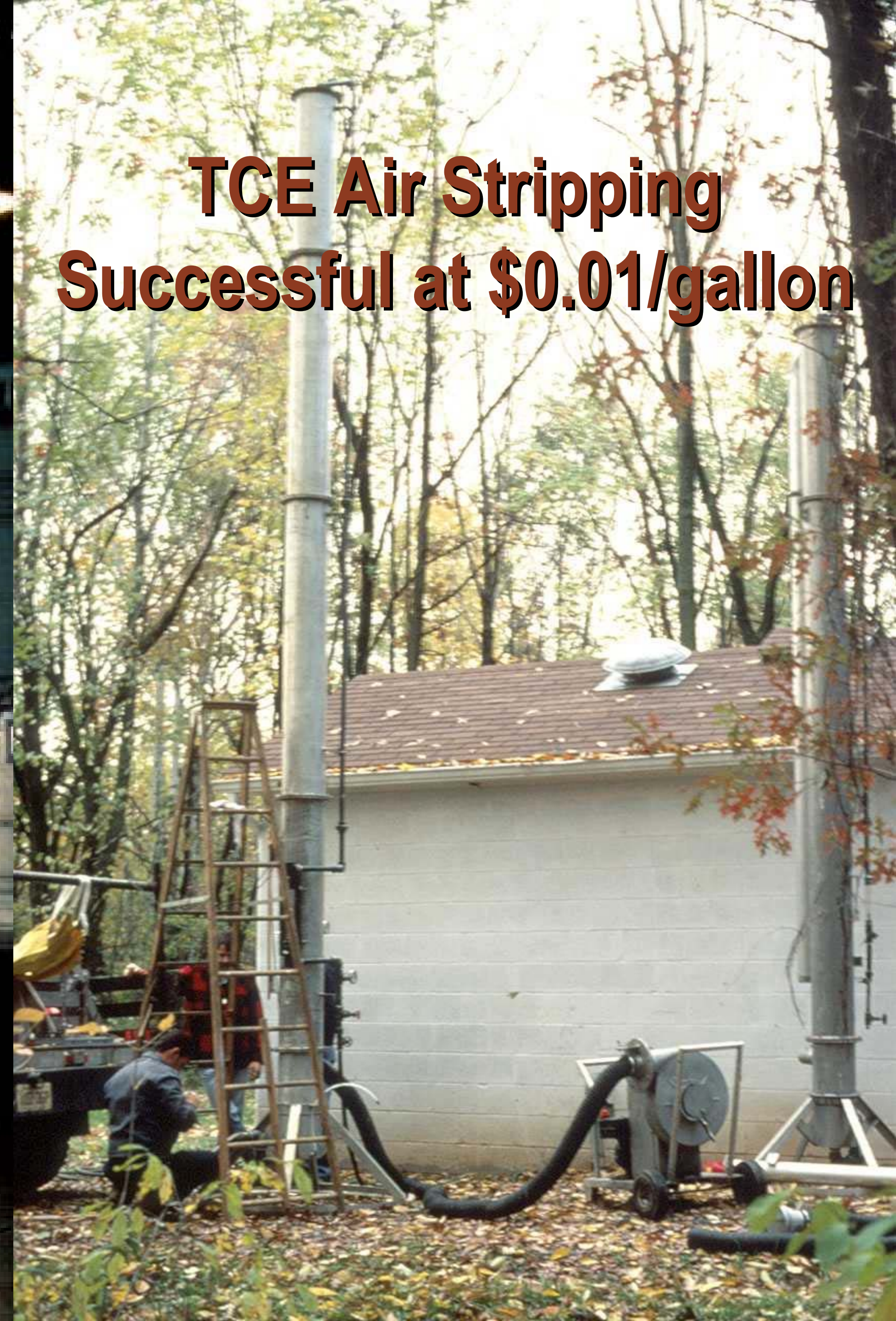


<u>Hydrogen Peroxide as an Oxygen Source</u>

- Too expensive
- Too unstable
- Too hazardous
- Is still sometimes used today in select applications

Introduction: Science vs. Technology





Remediation

- Where does our business fit into the science-to-technology model?
- Is it based on the "Bike" model of technology evolution?
- Hypothesis:
  - The rush to cleanup has forced us to skip most of the science in favor of the technology evolution model.
  - We tend to do the science when the technology doesn't perform as expected (intuitively) or independently of the technology.
  - When we learn/apply science, the actual technology performance is different than expected (counterintuitive).

What This Means to the RPM

- The RPM is in a unique situation. You have to make decisions based on available data. You want to make the best decisions you can, but you know there is always uncertainty.
- You are stuck between:
  - **Vendors** who want to sell you something.
  - **Regulators** who are trying to enforce laws and regulations.
  - **Management** who rarely understand the complexities and uncertainties of this business.
  - **The public** with a legitimate concern, but without a technical understanding of the problems.
- Your job is to make the best of the uncertainties and make the best decisions possible.

Presentation Overview

- Introduction: Science vs. Technology
- Plume Treatment
  - Introduction
  - Pump-and-Treat (P&T)
  - Monitored Natural Attenuation (MNA)
  - Permeable Reactive Barriers (PRBs)
  - Phytoremediation
- NAPL Source Zone Treatment
- The DNAPL Problem
- Summary and Conclusions

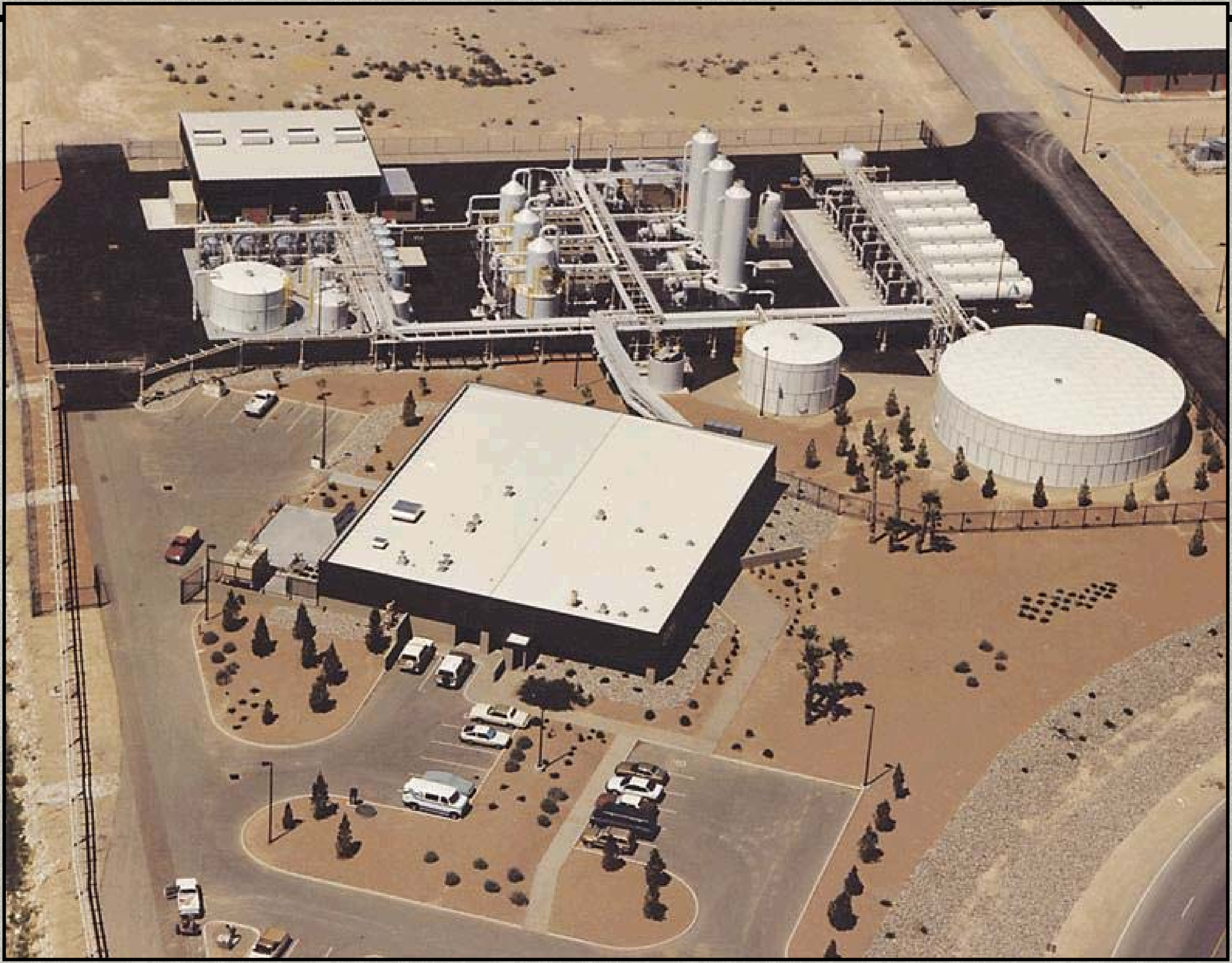
Introduction to Plume Treatment

- The source zone is defined as the area which has been in contact with nonaqueous-phase liquid (NAPL).
- The plume is the contaminated groundwater emanating from the source.
- Distinguishing the source and plume is not always easy.
- In the earlier years this distinction was not generally understood.
- Some technologies and lessons learned are applicable to either the source or the plume.

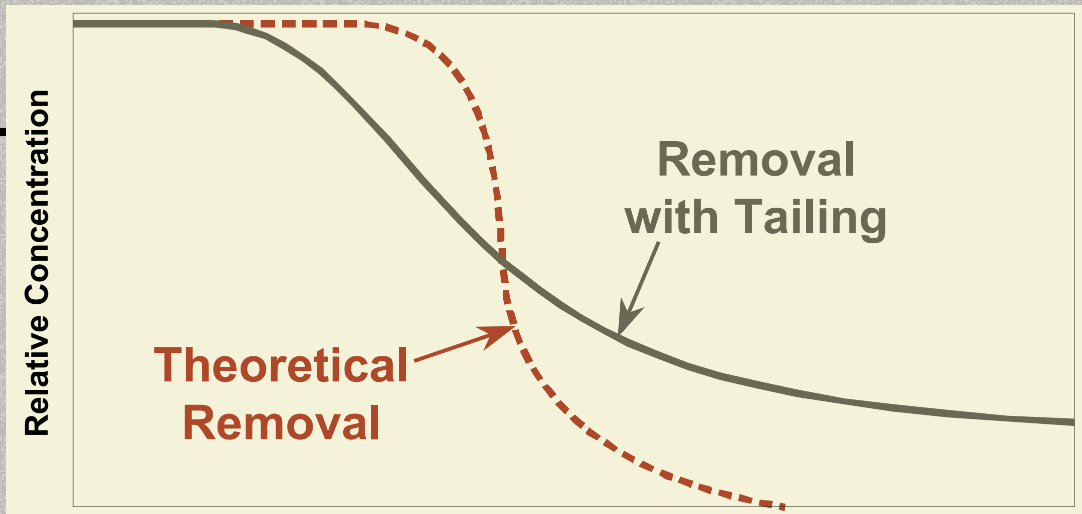
What We Thought In The '80s

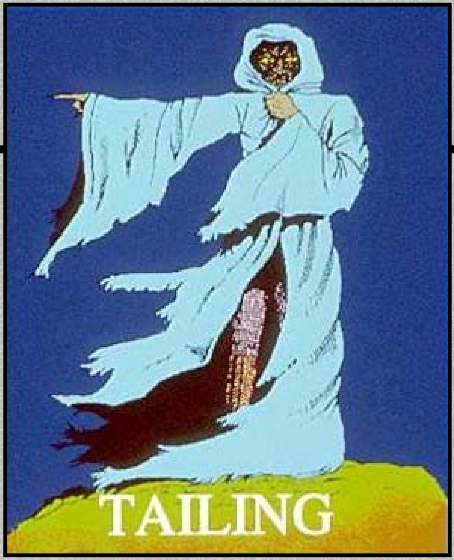
- We can actually clean up sites by pumping reasonable amounts of water over reasonable amounts of time.
  - 10- to 12-year design life was common
- Once we shrink the plume, it won't rebound.
- There really are no other options.
- P&T can't do any harm.

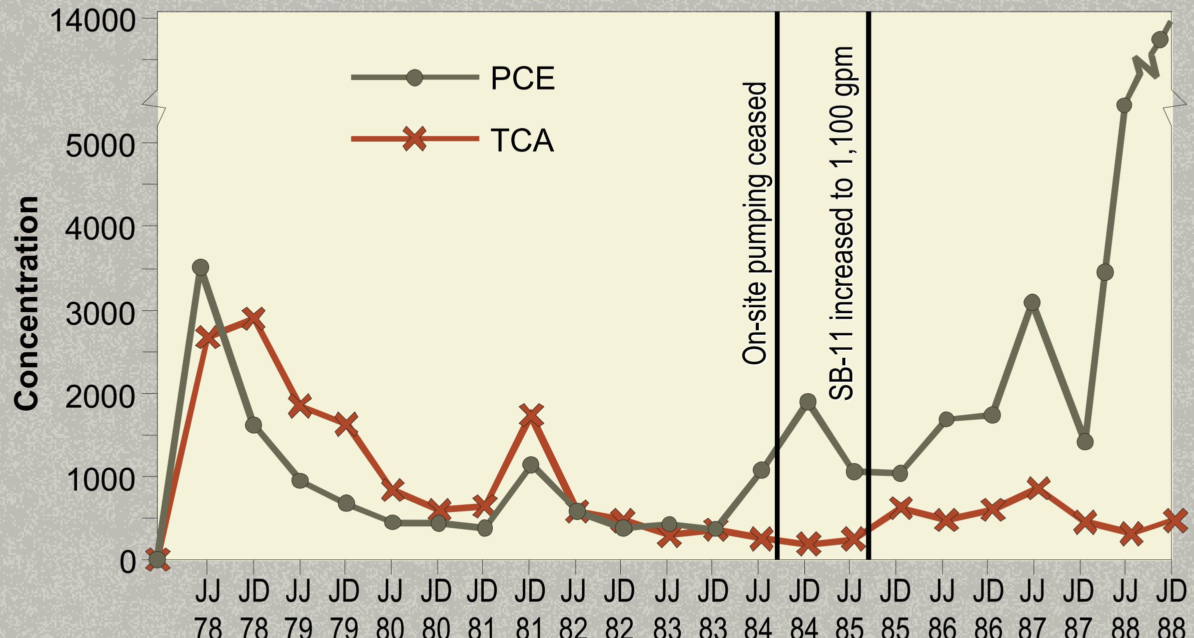
USAF Plant



Tailing and Rebound: The Evil Twins







Source: Parsons

What We Know Now

- Few sites have been cleaned/closed by P&T.
- By the late '80s and early '90s, P&T was in disfavor.
- P&T is now considered a containment technology and in that role is experiencing a comeback.
- Newer technologies now compete with P&T as containment technologies:
  - Monitored natural attenuation (MNA)
  - Permeable reactive barriers (PRBs)
  - Phytoremediation

What the RPM Needs to Know

We do have reasonable technologies for plume containment:

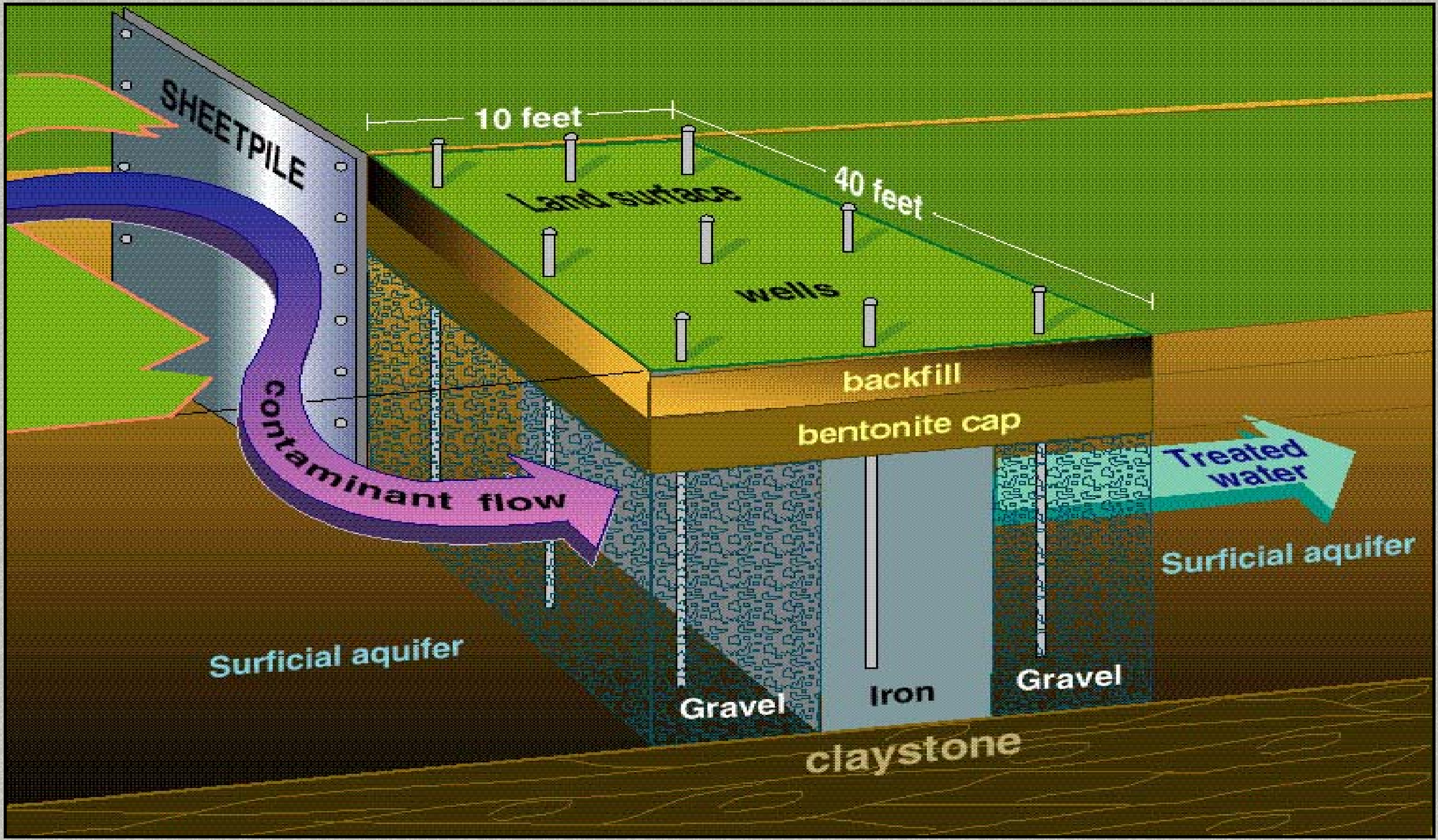
- P&T
- MNA
- PRBs
- Phytoremediation

Plume treatment remains more problematic.

MNA Applications and Limitations

- We do not have good techniques for estimating the time for remediation to MCLs.
- At many sites, chlorinated solvent plume stability is hard to demonstrate.
- We do not have much consistency in regulatory requirements for the application of MNA.
- Public perception and level of understanding may be poor.
- MNA is not appropriate technically at some sites.
- MNA is applicable to being used at hundreds of sites.

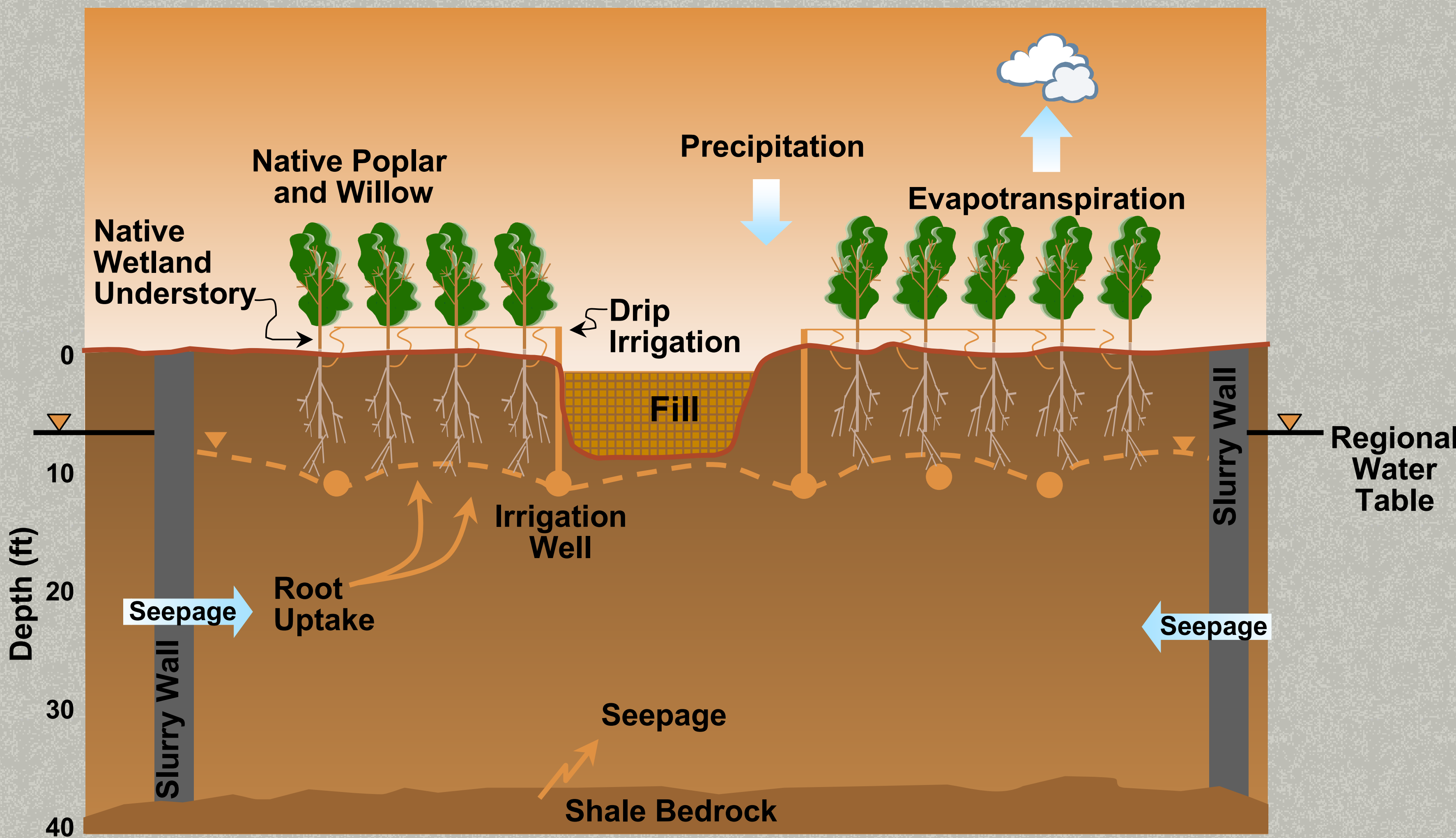
Conceptual Diagram



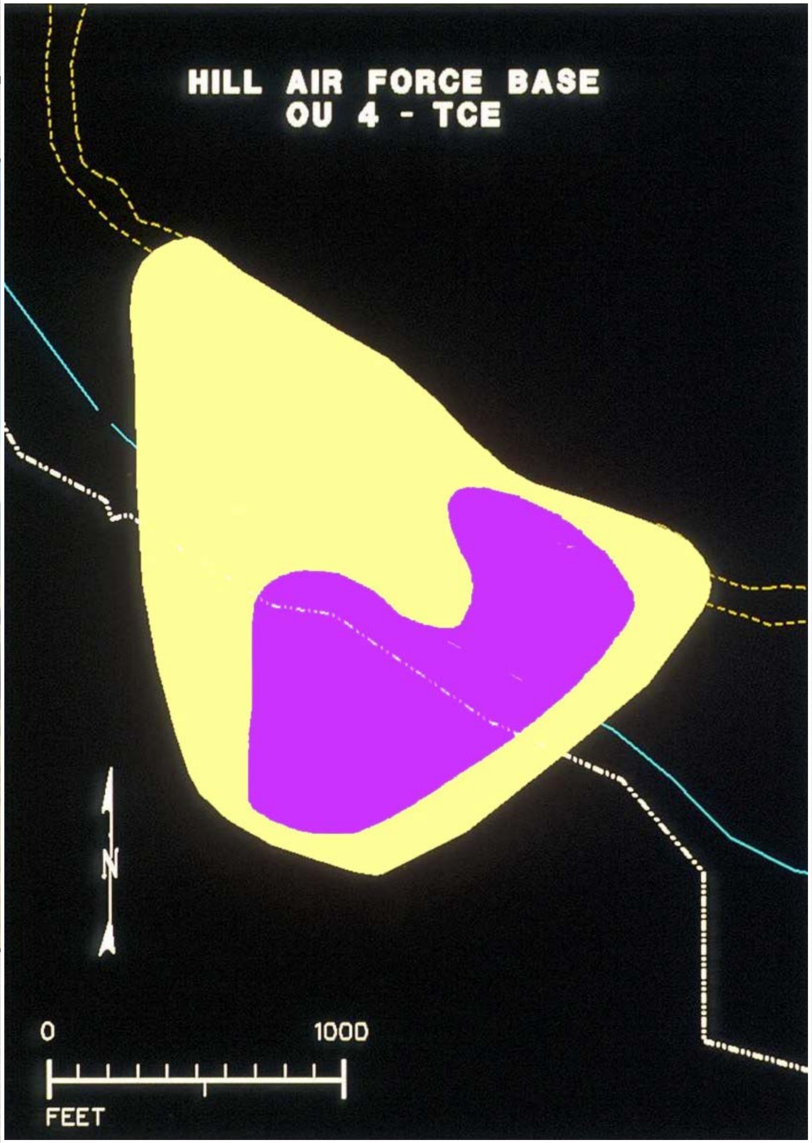
PRB Applications and Limitations

- Iron fouling, originally thought to be a problem, is not.
- The reaction occurs predictably and well.
- Primary reason for failure is that water often flows over, under, around, but not through:
  - Groundwater hydraulics not well understood at the time of installation
  - Barrier not deep enough
  - Barrier not long enough
  - Installation problems leading to bridging
- PRBs are being effectively used.

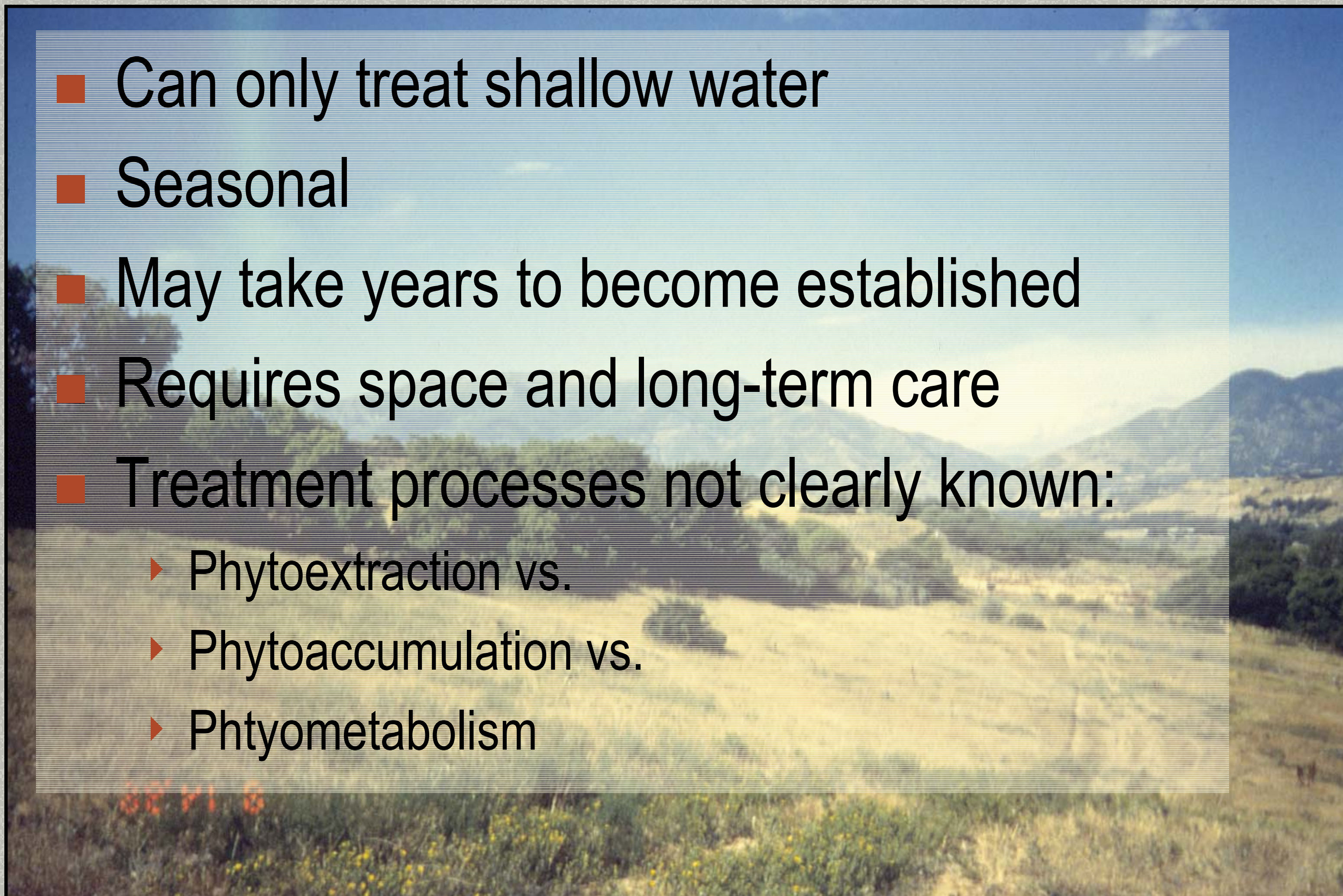
Conceptual Diagram



Natural Phytoremediation Example



Phytoremediation Applications and Limitations



- Can only treat shallow water
- Seasonal
- May take years to become established
- Requires space and long-term care
- Treatment processes not clearly known:
  - Phytoextraction vs.
  - Phytoaccumulation vs.
  - Phtyometabolism

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- NAPL Source Zone Treatment
  - Introduction
  - Groundwater Circulation Wells (GCWs)
  - LNAPL Free-Product Removal
  - In Situ Air Sparging (IAS)
  - Bioremediation
  - In Situ Thermal Treatment
  - In Situ Oxidation
  - Surfactant-Enhanced Aquifer Remediation (SEAR)
- The DNAPL Problem
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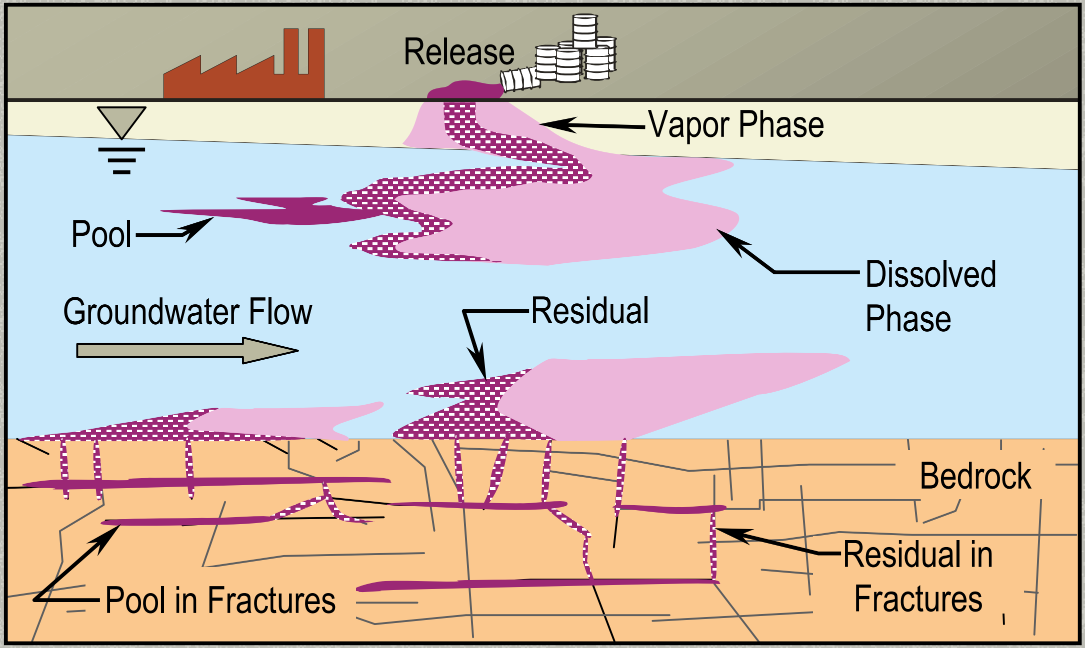
Introduction to Source Zone Treatment

- As stated earlier, the source zone is defined as the area directly impacted by NAPL.
- Source zone treatment technologies can be generally broken into 2 categories:
  - **Mass reduction** technologies are intended to remove a substantial portion of the NAPL mass, thereby measurably reducing the time to reach MCLs as compared to MNA
  - **Containment** technologies are intended to reduce or eliminate flux to groundwater, but will not measurably reduce time to reach MCLs as compared to MNA

Source Zone Contamination Phases

- Pooled DNAPL (mobile)
- Residual DNAPL (non mobile)
- Diffused into low-permeability materials (rock or soil)
- Sorbed to solids



What We Thought in the Mid-'80s

Mass Reduction/Source Removal Technologies

- Solvent source removal is difficult, but it is always good, and will always reduce risk.

What Some People Think Now

Mass Reduction/Source Removal Technologies

Solvent source removal is too tough

- Models and experience show that you have to get nearly all of it in order to make a significant difference on plume length and concentration over a time-frame measured in decades.

What We Still Don't Know

Mass Reduction/Source Removal Technologies

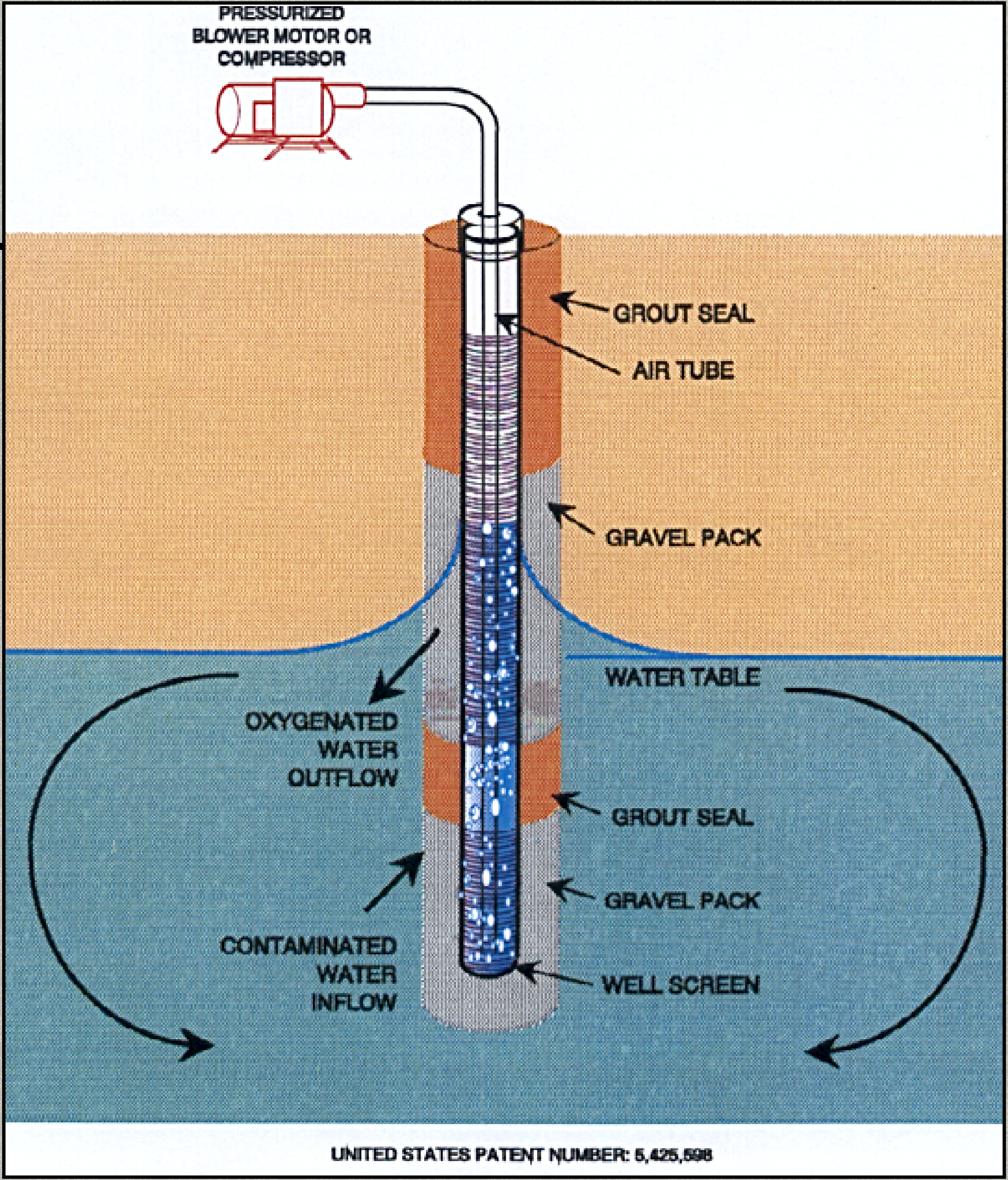
The Debate

- Do complicated source removals pass the cost/benefit test?

Groundwater Circulation Wells (GCWs)

- Developed in Germany
- Brought to the U.S. in the early '90s
- Also known as:
  - NoVocs
  - Recirculation wells
  - Density Driven Convection (DDC)
  - In-well aeration or air stripping
  - UVB
  - KGB
  - Etc…..

Conceptual Diagram



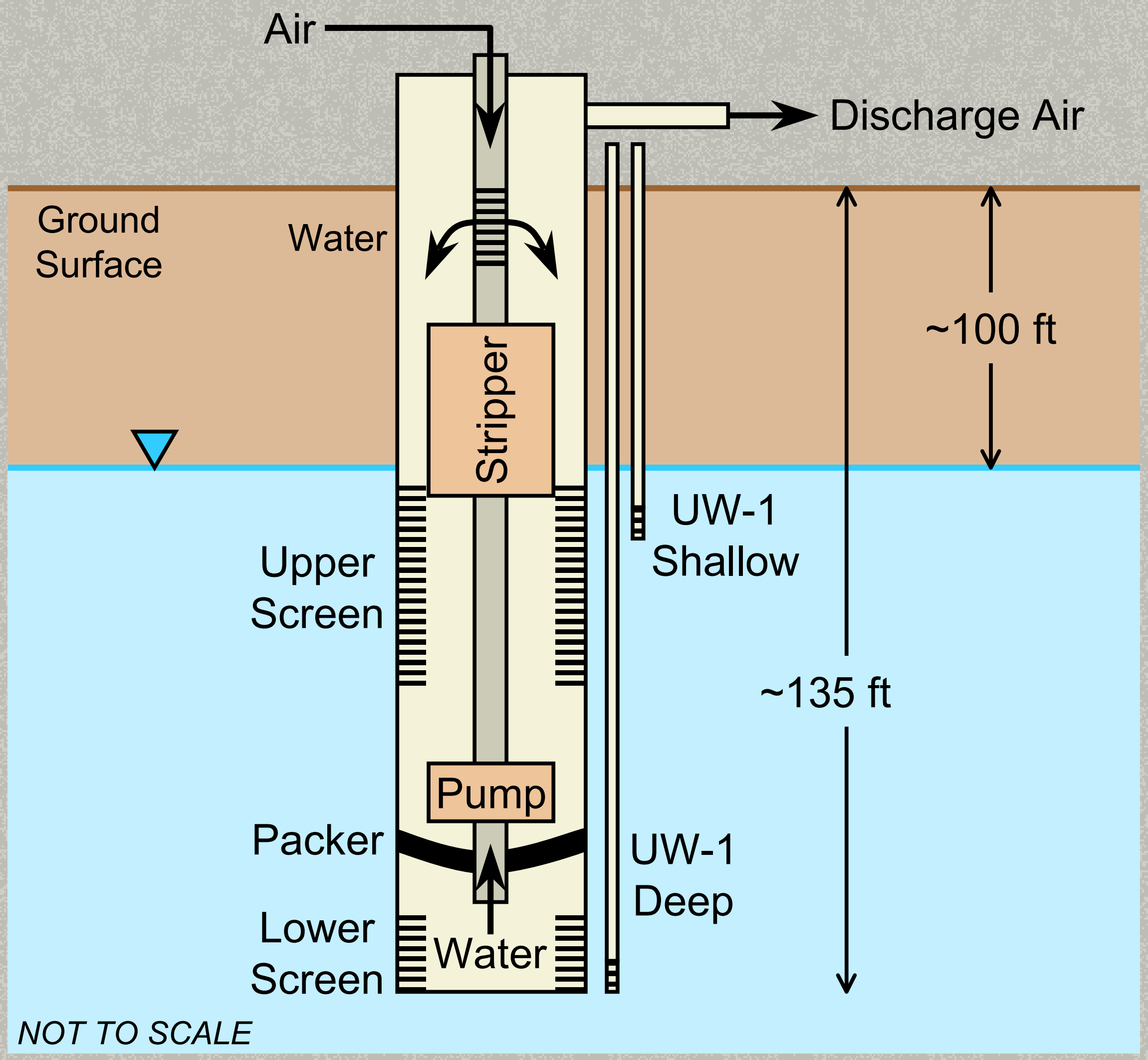
What We Thought (and What Vendors Claimed) in 1991

- More Effective Than P&T
- Lower Cost Than P&T
- Fewer Wells Than P&T
- Lower Energy Requirements Than P&T
- All Components Below Ground
- Permitting Advantages Over P&T

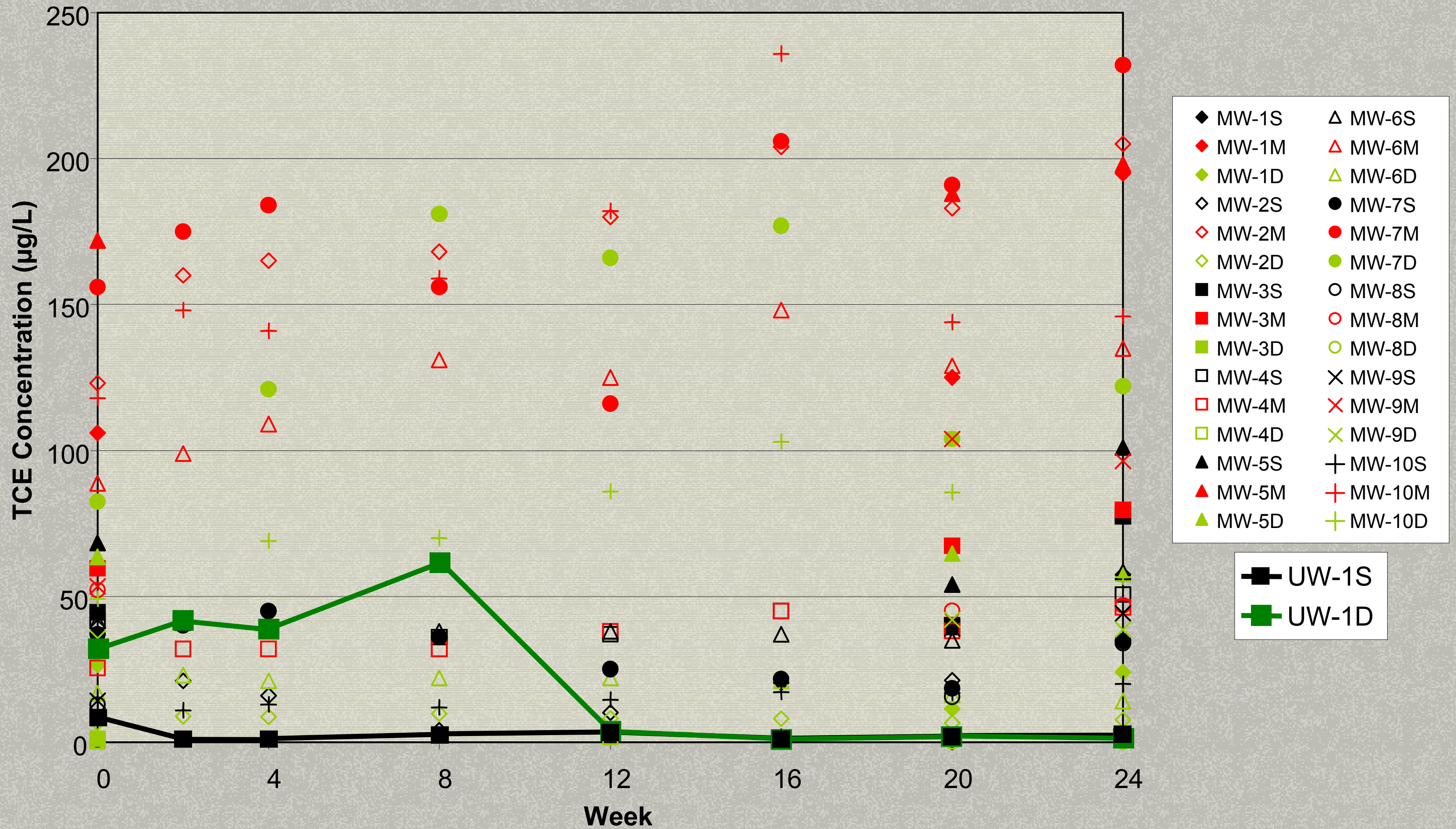
Demonstration Sites

- Cape Canaveral Air Station
- Edwards AFB
- Hill AFB
- Keesler AFB
- March AFB
- Massachusetts Military Reservation (MMR)
- North Island NAS
- Oceana NAS
- Port Hueneme
- Tyndall AFB
- Yuma MCAS
- Others

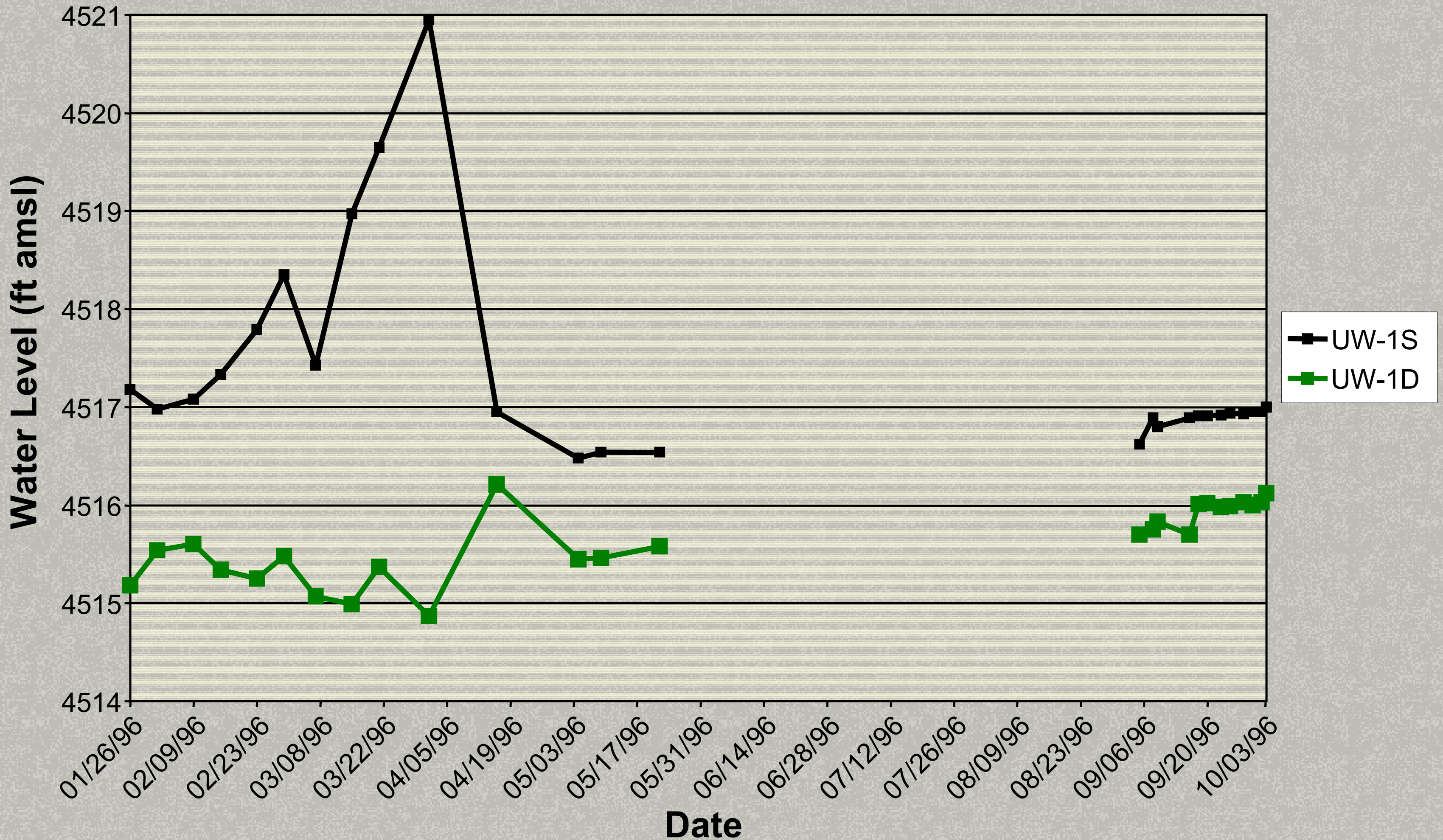
UVB Well Construction



TCE Concentrations Measured During the UVB Test



UVB Monitoring Well Water Levels

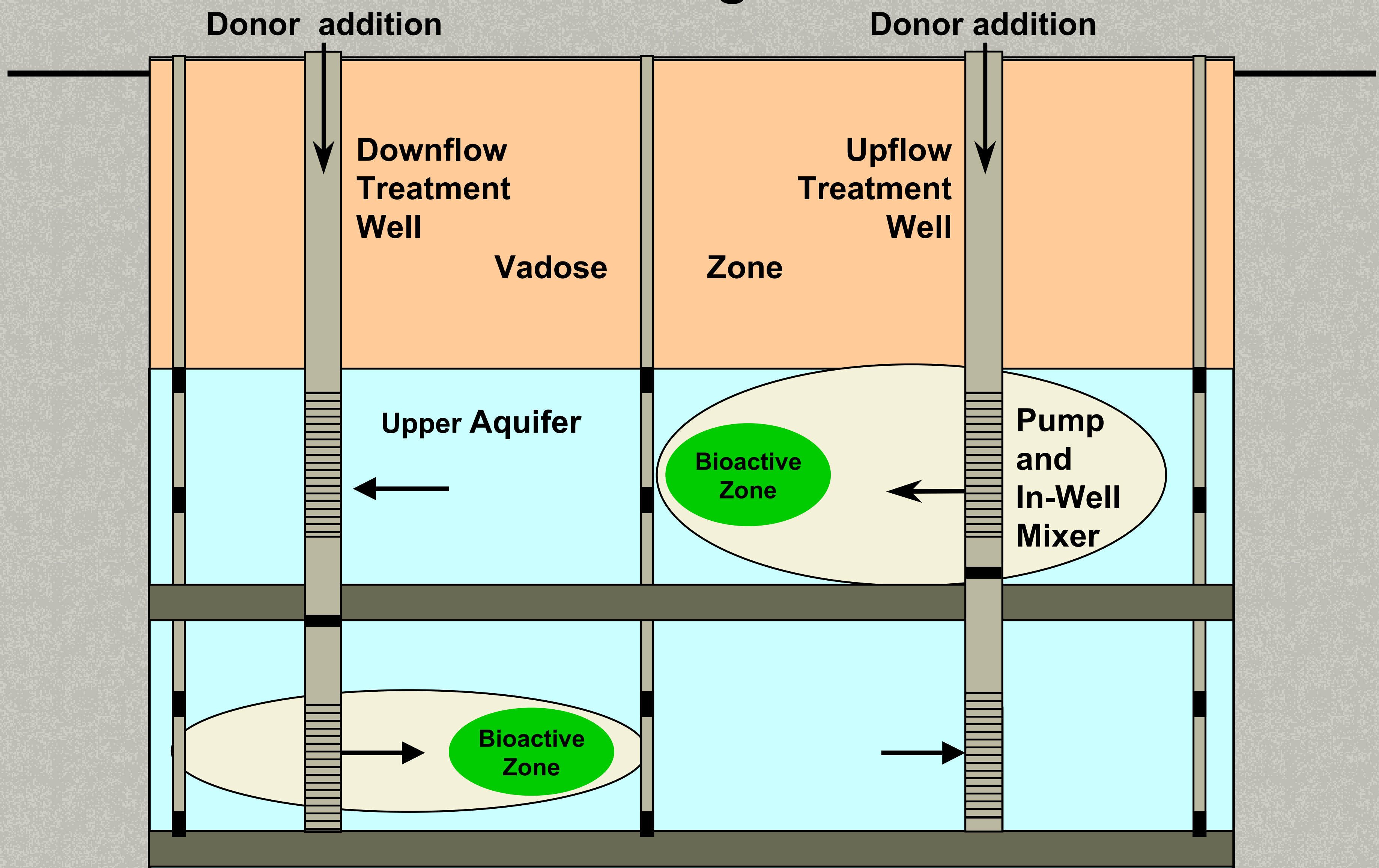


"What we got here is a failure to recirculate ...(aka, pump and no treat)"

Demonstration Results

Claims	Demonstration Results
More Effective Than P&T	Not substantiated
Lower Cost Than P&T	Not substantiated
Fewer Wells Than P&T	Not substantiated
Lower Energy Requirements Than P&T	NO!
All Components Below Ground	Yes, but …
Permitting Advantages Over P&T	Yes

In Situ Mixing Well Pair



What the RPM Needs to Know

- GCW technology has proven difficult to apply in a cost-effective and useful way; despite 10+ years of trying, many concerns remain.
- GCW technology intuitively appears to offer advantages that have not been proven by experience.
- If the GCW technology is considered for application, the RPM needs to recognize the risks of failure and limitations on monitoring.
- In one form or another, GCWs are probably here to stay!

LNAPL Removal – What We Thought in the '80s

- The amount of product observed in a well was related to the total amount recoverable.
- Product would flow to wells and/or trenches where it could be pumped out.
- A significant amount of the total contamination could be removed by removing the liquid portion
- Removal of product was always good and would reduce risk.

Conclusions from 44 Pilots

- Free product recovery is unpredictable!
  - The feasibility of free product recovery must be determined in the field with focused testing
- The avoidance of one bad product recovery system ($250K) pays for more than five pilot tests ($35-56K/test).
- Use mobile equipment where possible. Free product recovery is a risky, short-term undertaking.
- 5-10% (Realistic); 30% (Maximum) of free-product is recoverable via liquid-phase recovery.

Bioslurper system used to remove both liquids and vapor at Fallon NAS, NV

What We Know Now

- For most sites, little product will flow to wells/trenches by gravity alone.
- Little relationship exists between product in a well and the amount "floating" on the water table.
- Removable free product represents a small fraction of total contamination at most sites.
- Only 7 of 44 sites tested with vacuum-enhanced removal produced even interesting amounts of product.
- We still don't know how to accurately predict the volume of recoverable product without a pilot test.

What the RPM Needs to Know

- Free-product recovery is frequently required to some poorly-defined level.
- Free-product recoverability is difficult to predict.
- Most successful free-product recovery strategies involve an observational approach:

Bail down → Pilot → Incremental application

- Free-product recovery will have little impact on risk or on the dissolved plume.

In Situ Air Sparging – What Some Thought in the Early '80s

- Injecting air into the water was much like injecting air into the vadose zone (bioventing).
- Air would behave in porous media (aquifers) much like it did in water.
- Bubbles would be formed and they would strip contaminants from, and supply oxygen to, groundwater.
- We could design a system based on monitoring well and pressure data.

Some Quotes

~1990

"Air sparging is a rapid and effective way to clean groundwater."

– U.S. EPA

~1993

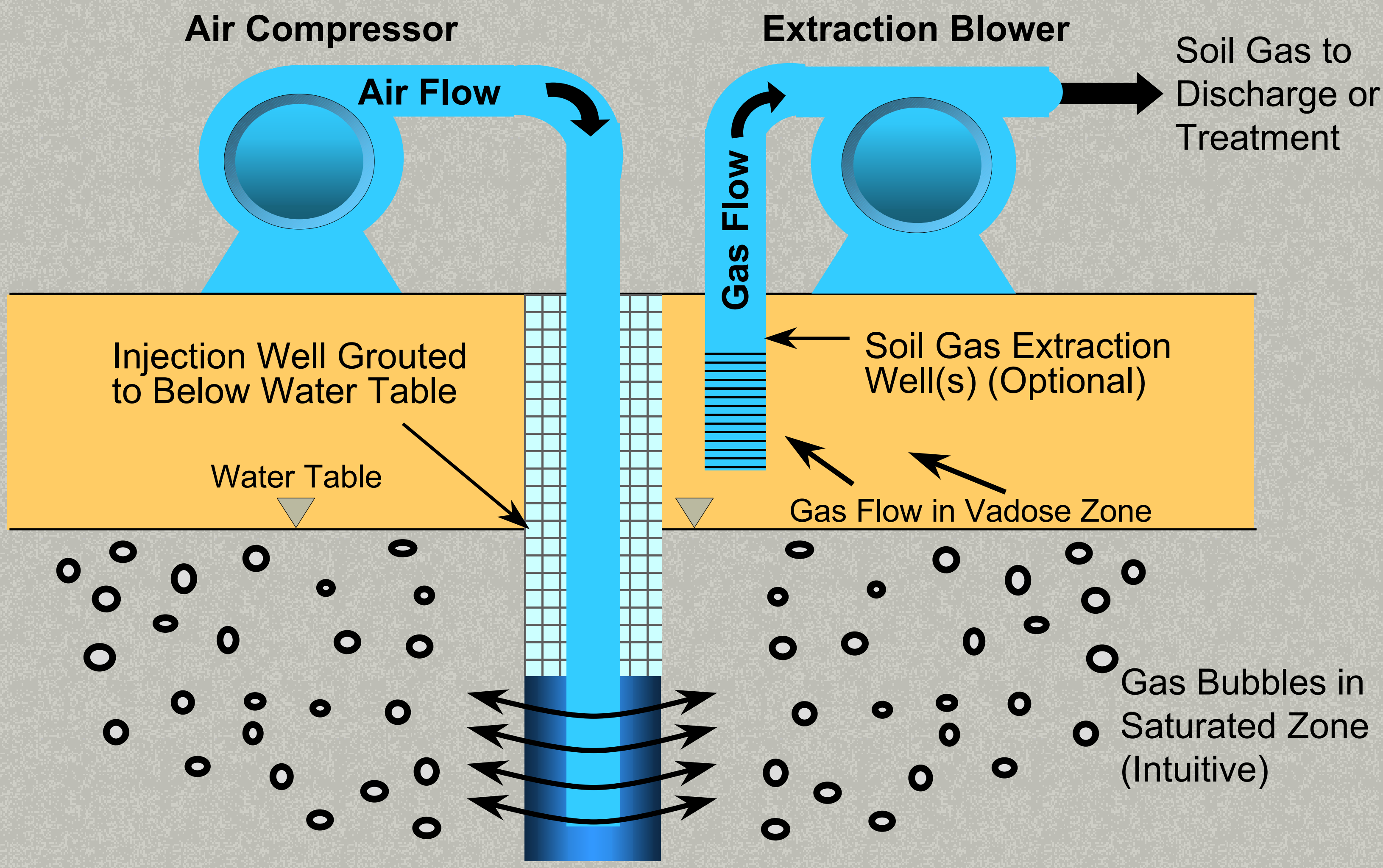
"Air sparging is the best technique we have for cleaning up monitoring wells." – Anonymous

~1995

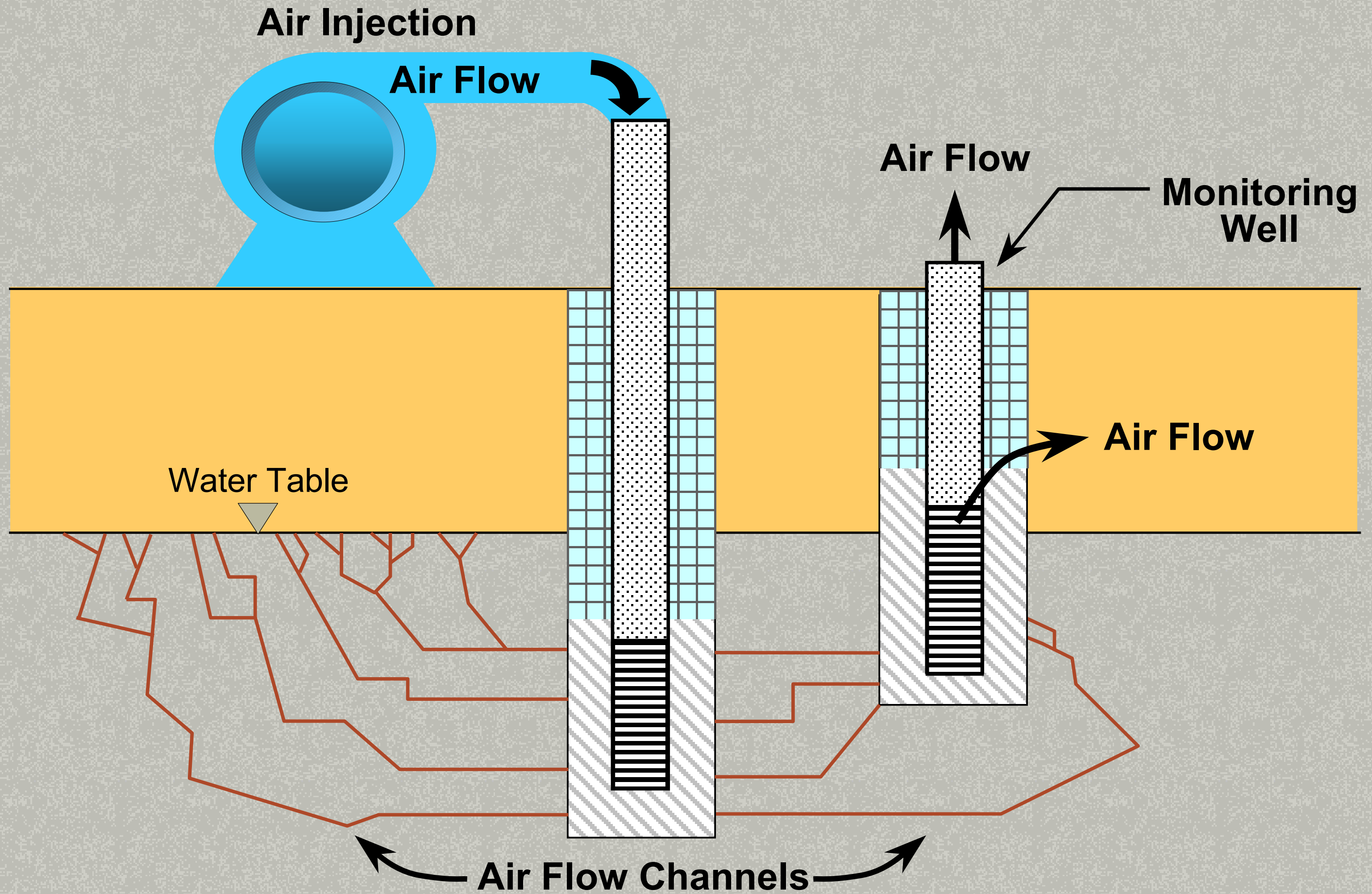
"Air sparging is the cheapest regulatory placebo."

– Anonymous

IAS Model – Early '90s



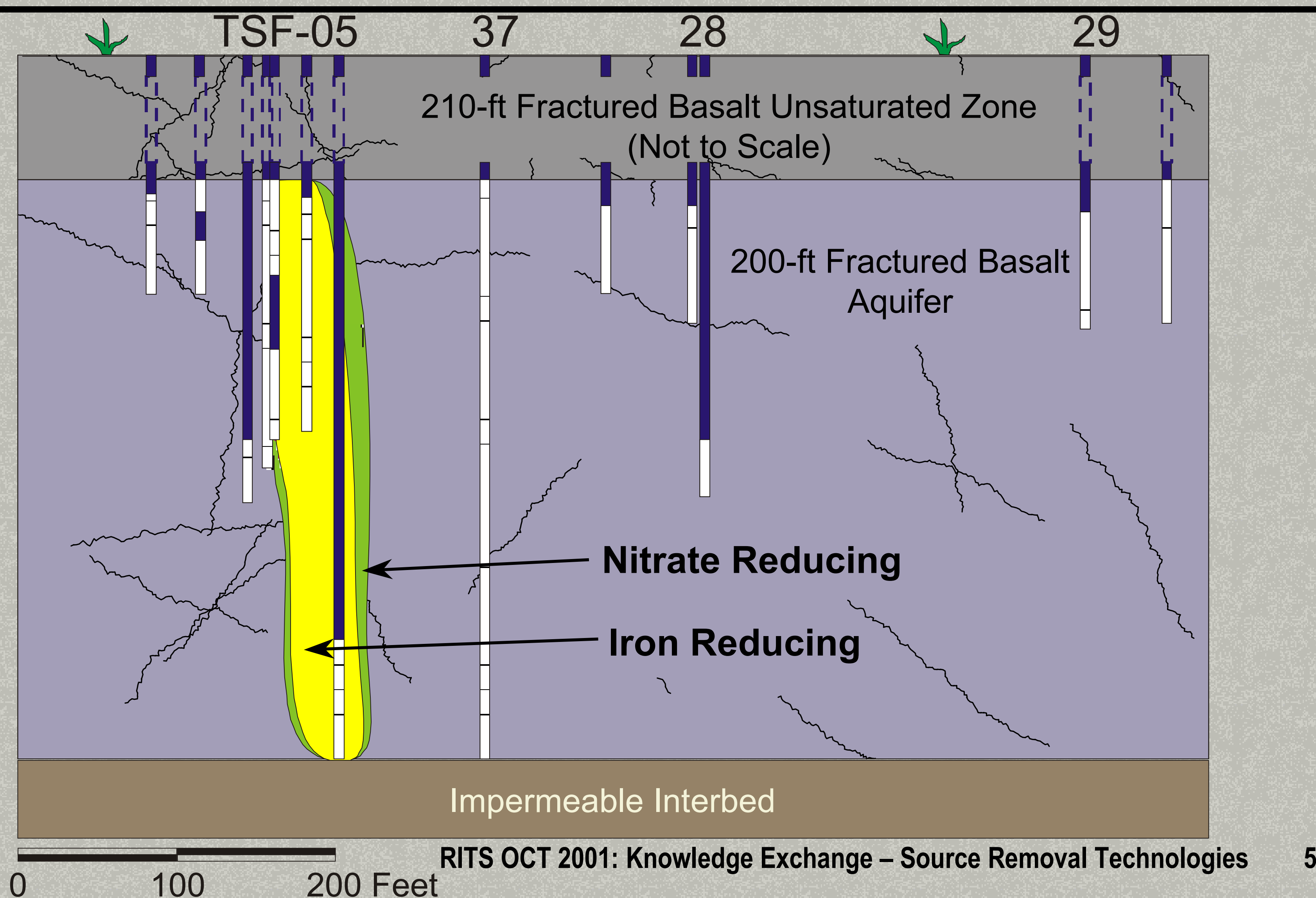
IAS Model – Now



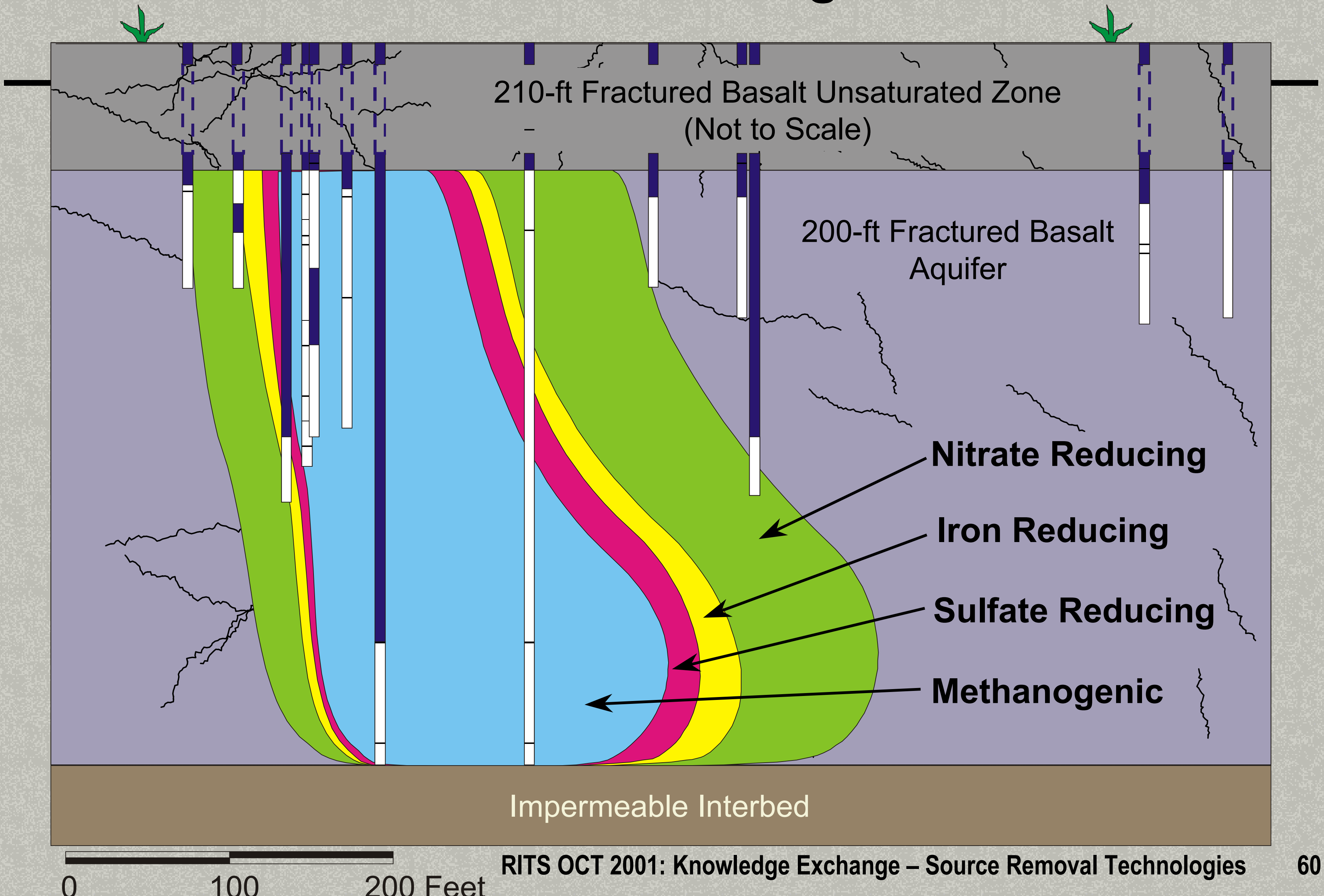
What We Know Now and What the RPM Needs to Know

- Bubbles are not formed, and air moves through a series of channels.
- Injecting air into the vadose zone and into water are totally different, the latter being hydrodynamically unstable.
- Basically 1 of 2 conditions exists:
  - Homogeneous conditions typically yield 2-m radius of influence
  - Nonhomogeneous conditions yield unpredictable flow
- In general, design of IAS is more art than science.
- IAS is frequently the low-cost source removal technology.

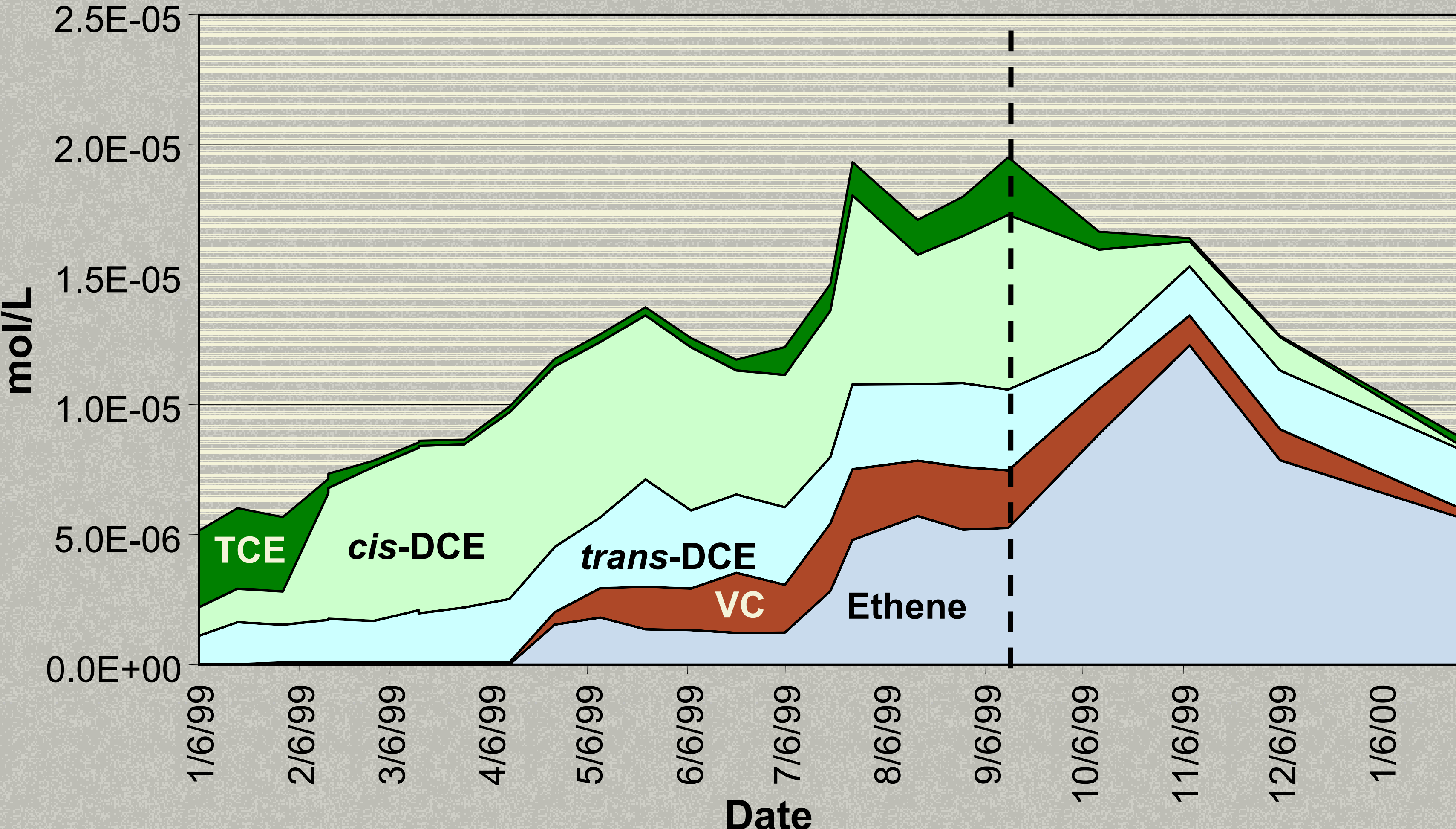
Initial REDOX Conditions



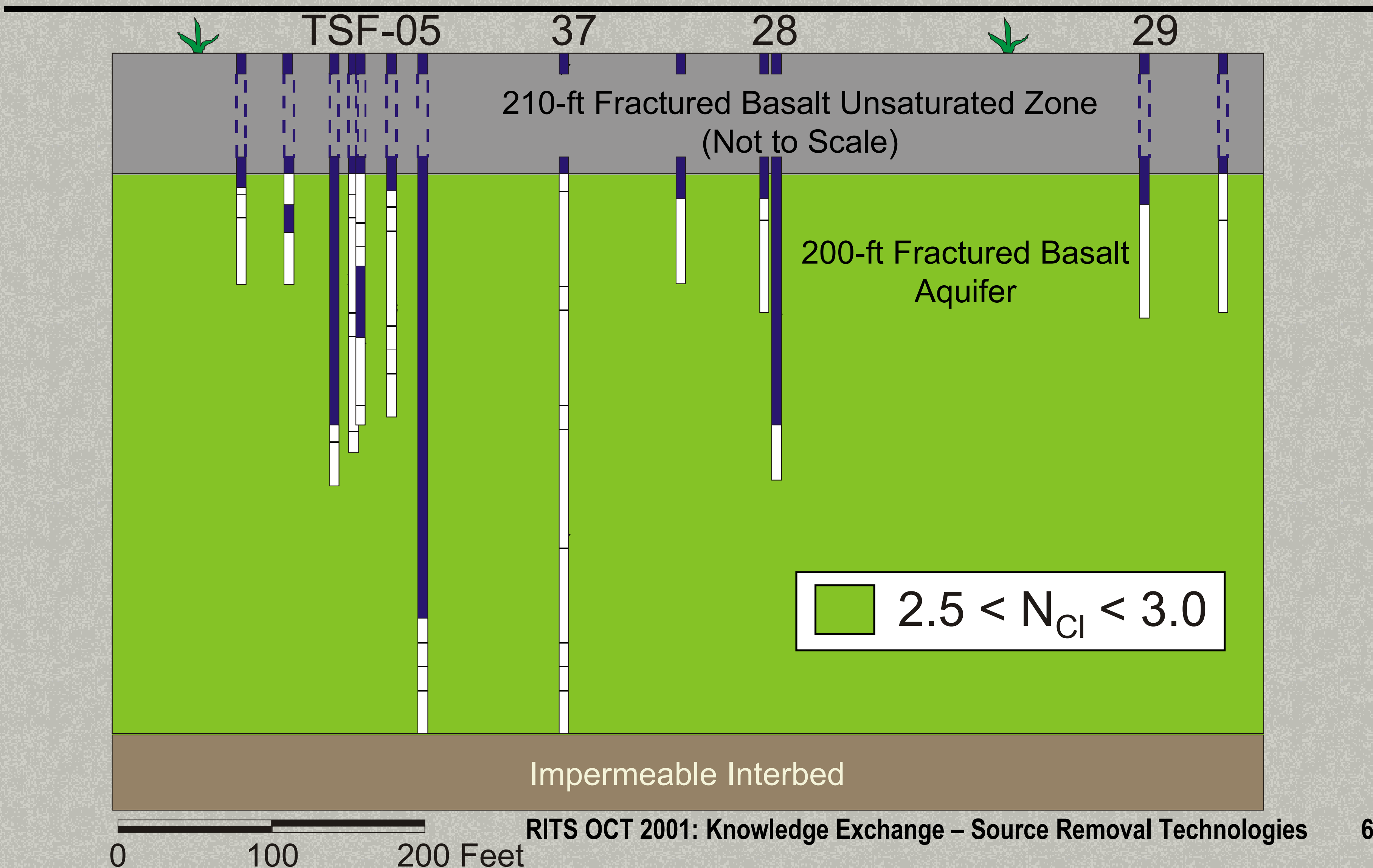
Redox Conditions Aug. 30, 1999



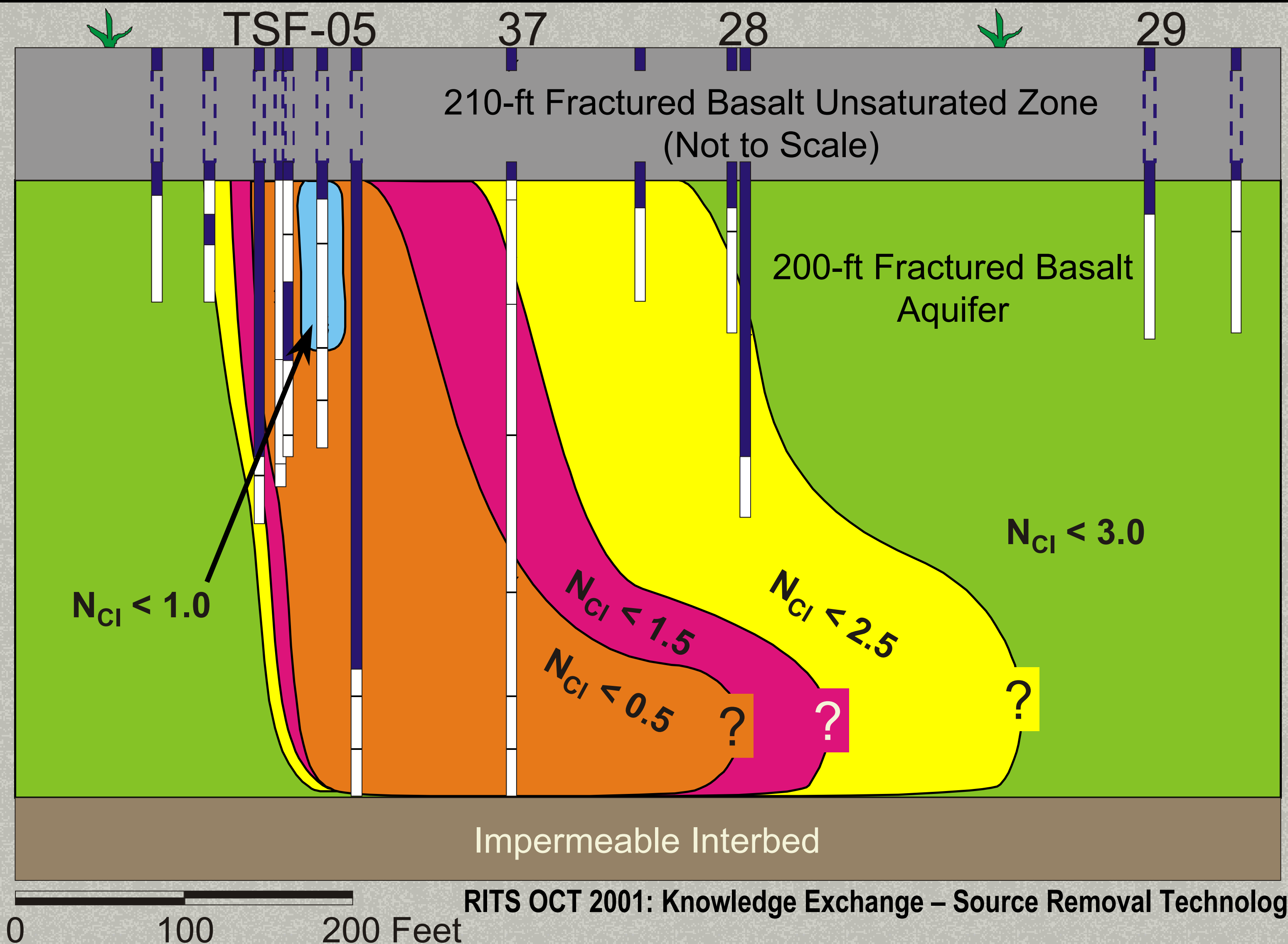
Reductive Dechlorination Indicators in TAN-25



Initial Chlorine Numbers

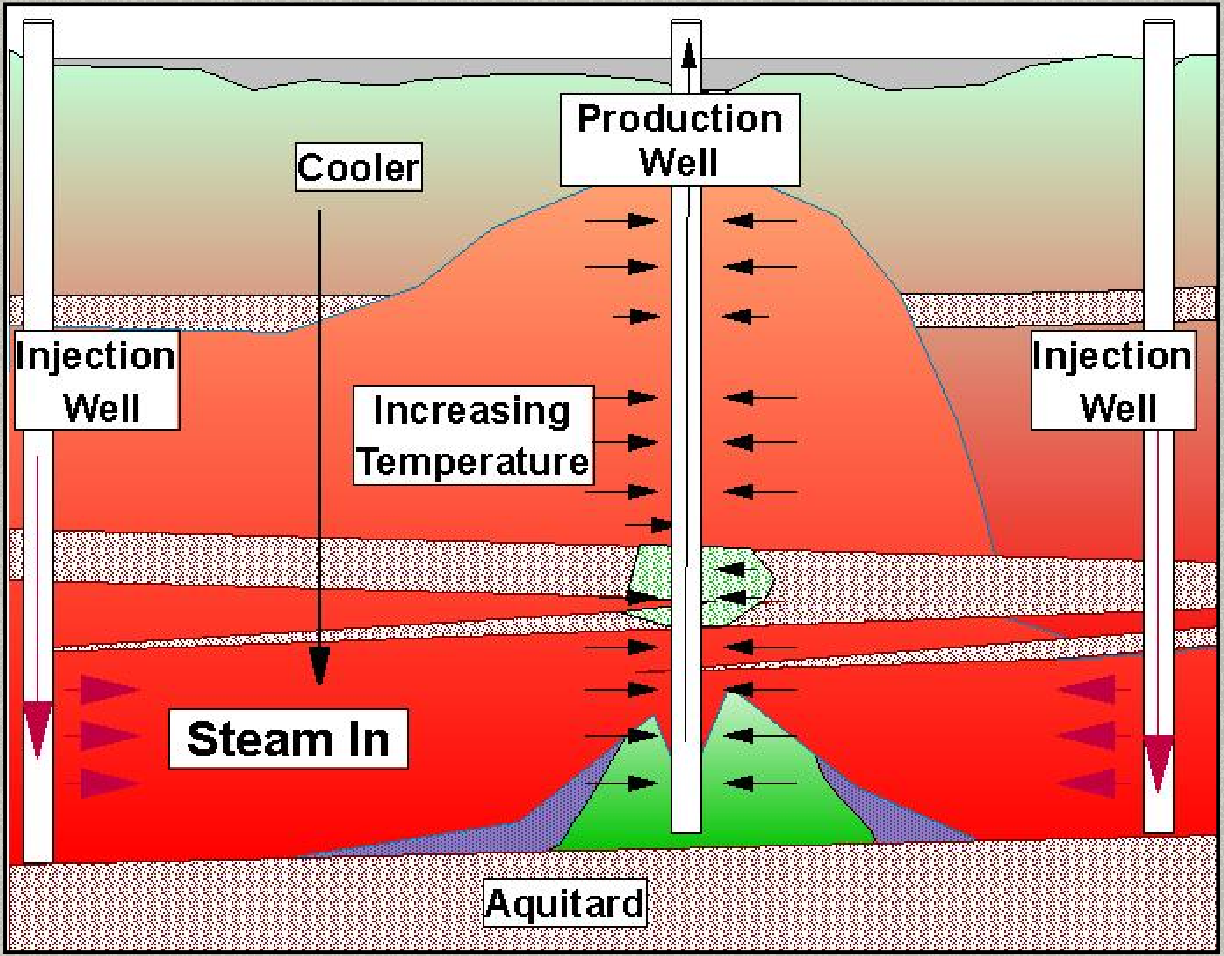


Chlorine Numbers Jan. 10, 1999



In Situ Thermal Treatment

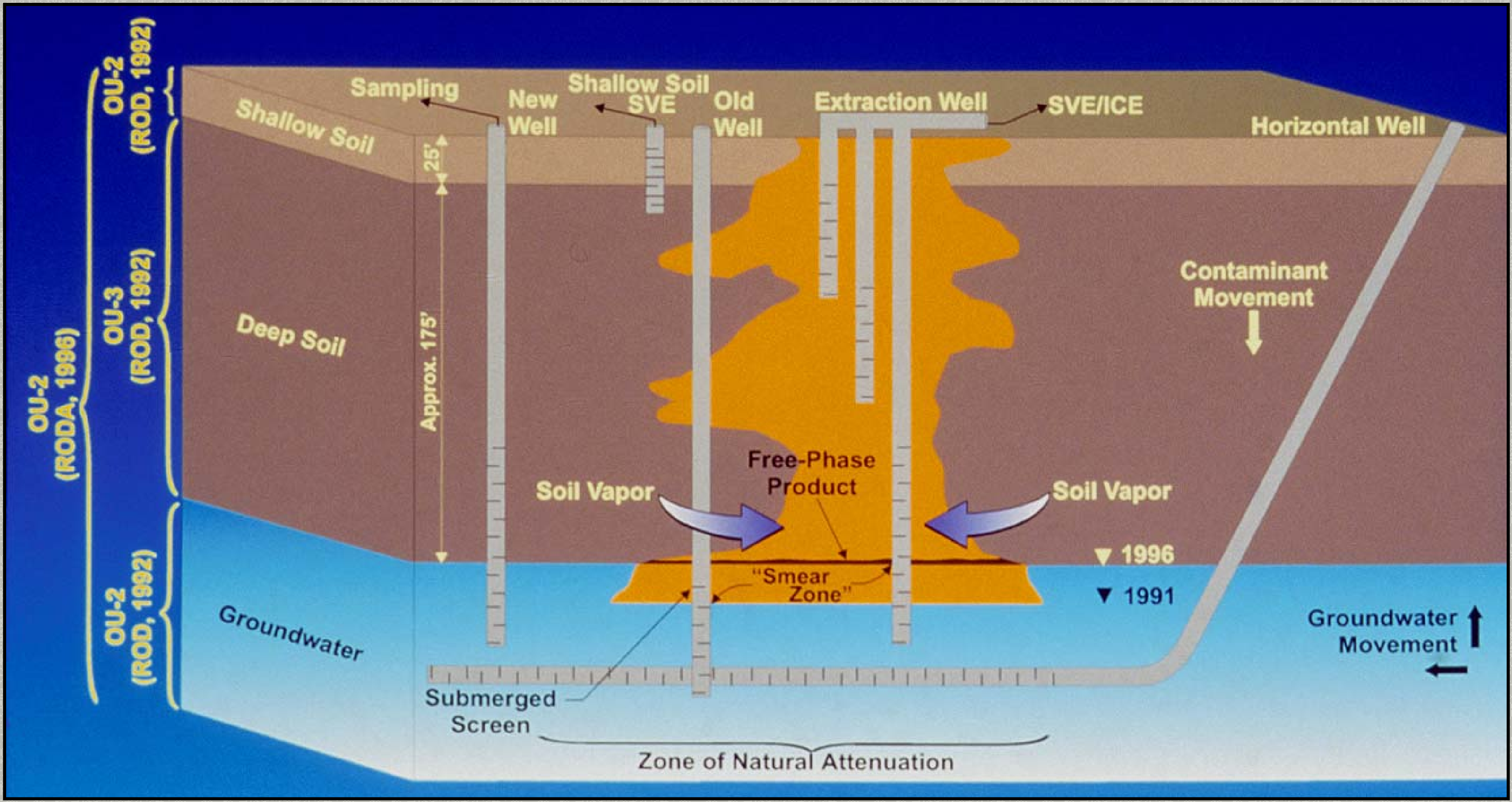
- Steam Injection
- Joule Heating
- Hot Well/ Thermal Blanket
- Radio Frequency Heating



Case Study – Williams, AZ

- Large LNAPL plume trapped below a rising water table
- Feasibility Study (FS) recommends conventional remediation plus MNA (MNA+) or MNA+ and steam injection
- The incremental increased cost of steam injection is $8,000,000
- An expert panel (Tiger Team) was assembled to address the issue
  - Roger Aines – Lawrence Livermore National Laboratory
  - Rob Hinchee – Battelle Memorial Institute
  - Paul Johnson – Arizona State University
  - Charles Newell – Groundwater Services, Inc.
  - Tom Sale – Colorado State University
- Is this an appropriate site for steam injection, or would the MNA+ alternative be better?

Conceptual Diagram



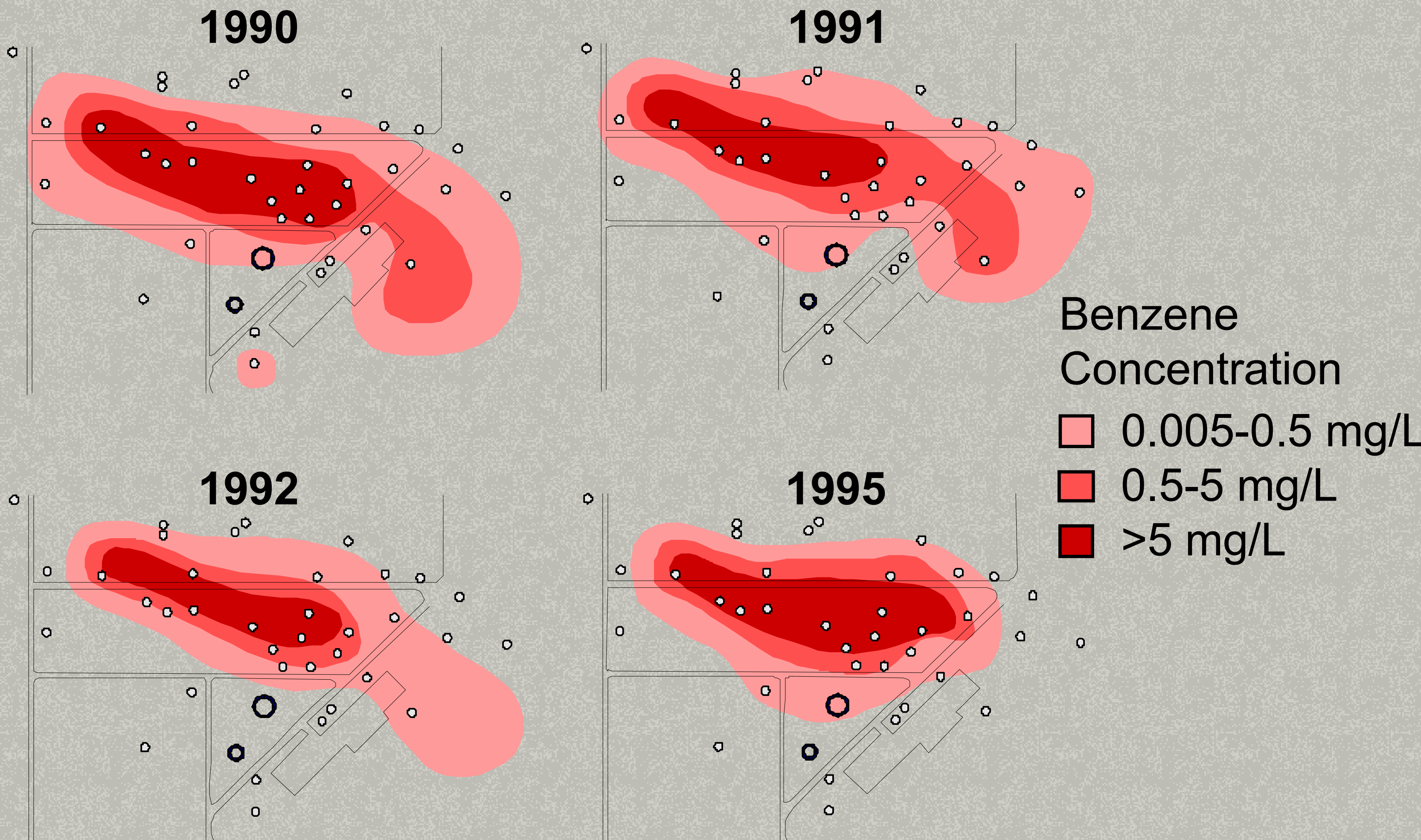
Question to Panel

Case Study – Williams, AZ

- What pilot testing should be done to evaluate steam injection?

Benzene Concentrations

Case Study – Williams, AZ



Time for the Aquifer to Reach MCLs

Case Study – Williams, AZ

With Steam Injection

Time to MCLs	100 yr	50 yr	30 yr	10 yr
Panelists Confident	100%	60%	20%	0%

Without Steam Injection (FS estimate)

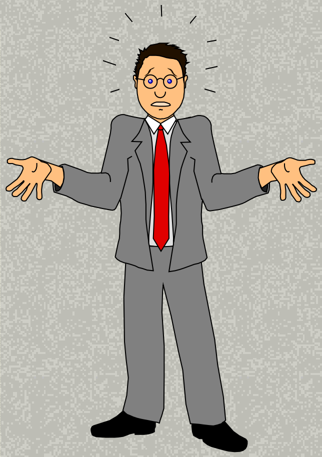
~ 500 years to reach MCLs

So What Do We Get for $8,000,000?

1. Mass removal today instead of biodegradation in the future.

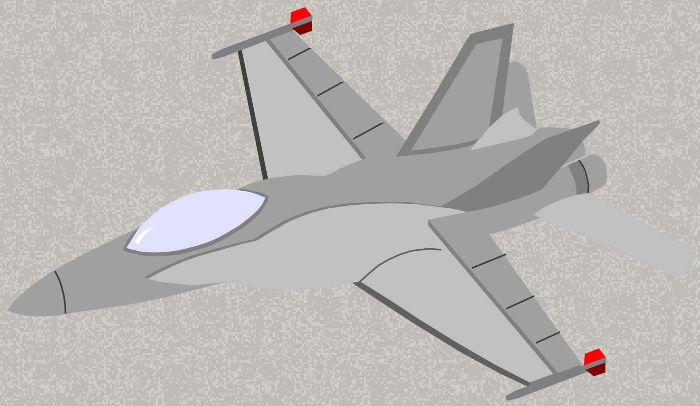
2. A cleaner site sooner, but not too soon.

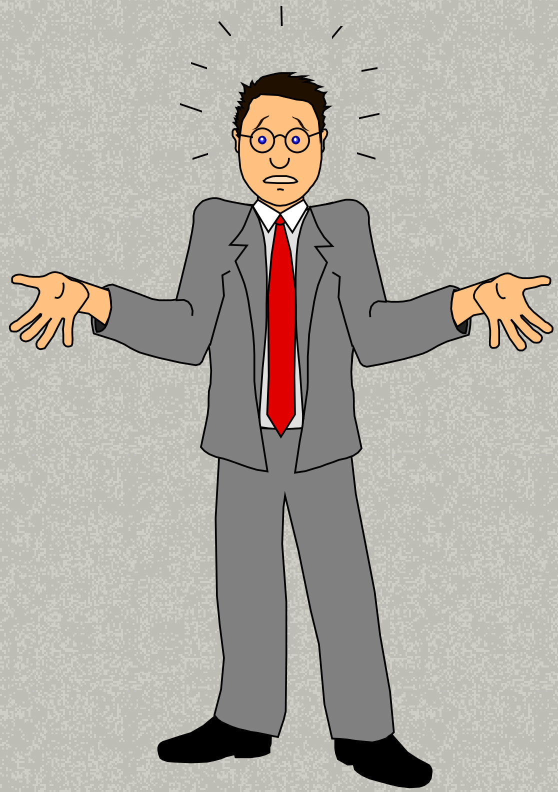
3. Less contamination, but probably not less risk, while we wait.

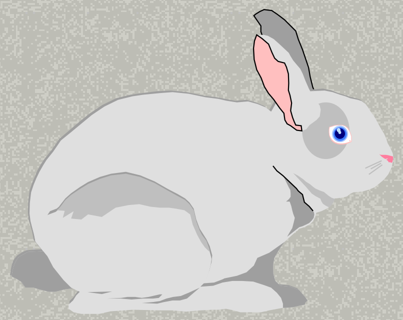


So What are You the Manager Going to Do?

Birds or Bunnies?







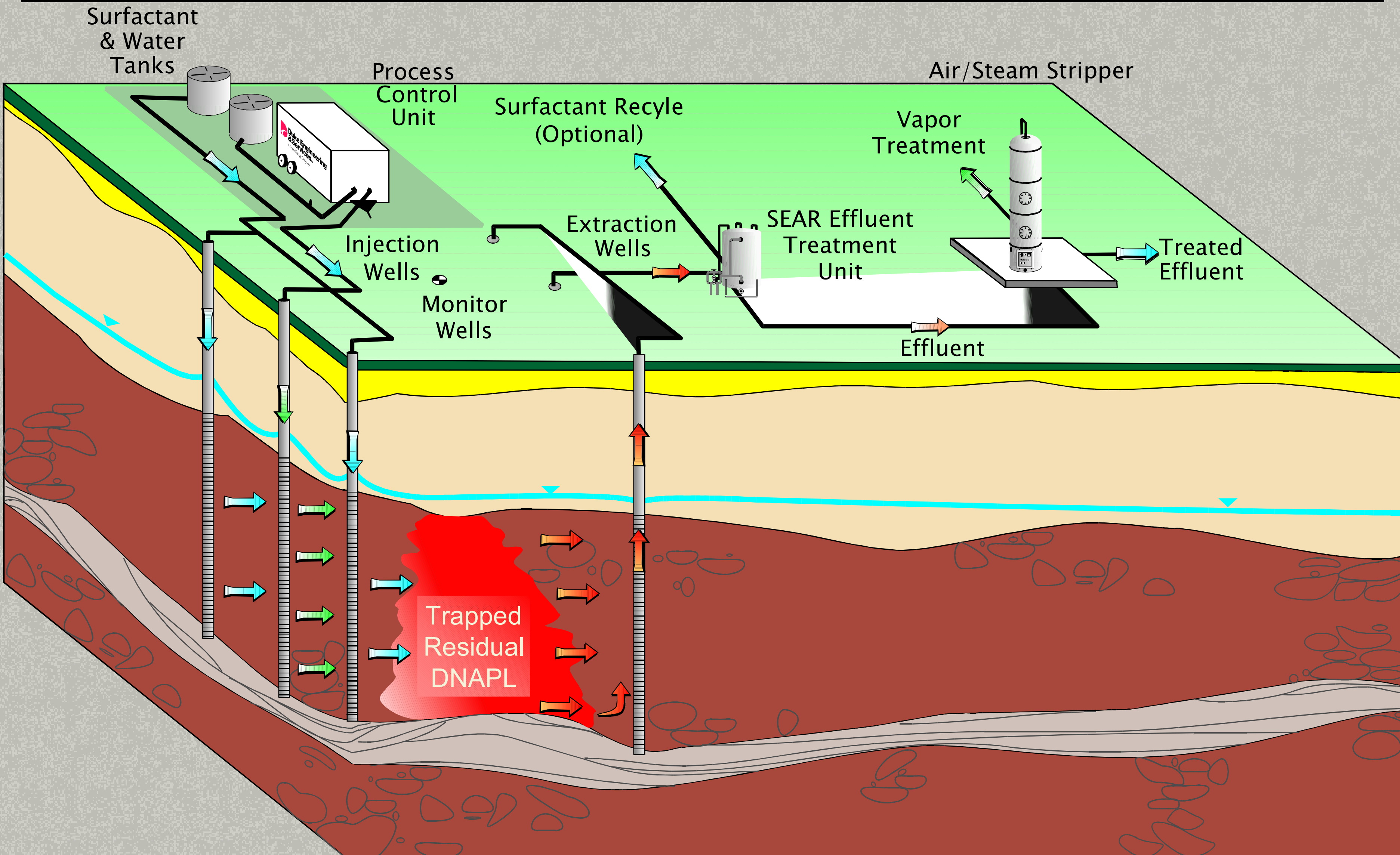
In Situ Oxidation

- Science tells us chlorinated compounds are easily oxidized.
- Practice tells us otherwise.
- ESTCP study of available case studies found only 1 of 13 applications where remedial objectives were completely met, and that was only on a small part of the site; significant rebound occurred 6 of the 7 times it was measured.
- As a result, SERDP has initiated more basic study.

NAPL Source Zone Treatment: SEAR

Surfactant-Enhanced DNAPL Recovery

Source: Duke Engineering



Applicability and Limitations

Surfactant and Other Enhanced Recovery Technologies Will Play a Role, but....

- The very effect that makes these technologies successful, reduction of interfacial tension – also increases the risk of downward movement.
- Aboveground treatment, surfactant cost, and recycling issues make this an expensive process.
- Residual dissolved concentrations in the aquifer may be problematic.
- Hill AFB is claiming something like 96% mass recovery.

A Tale of Two Sites: OU-2 and OU-6

OU-2 NAPL Plume

- 25 to 30 years old
- >40,000 gallons NAPL recovered
- Estimated >100,000 gallons residual NAPL
- Plume 2,100 ft long
- USAF is undertaking surfactant recovery with an estimated 96% efficiency

OU-6 TCE Plume

- >25 years old
- No NAPL recovered
- Estimated 50 gallon NAPL residual
- Plume 3,500 ft long

Presentation Overview

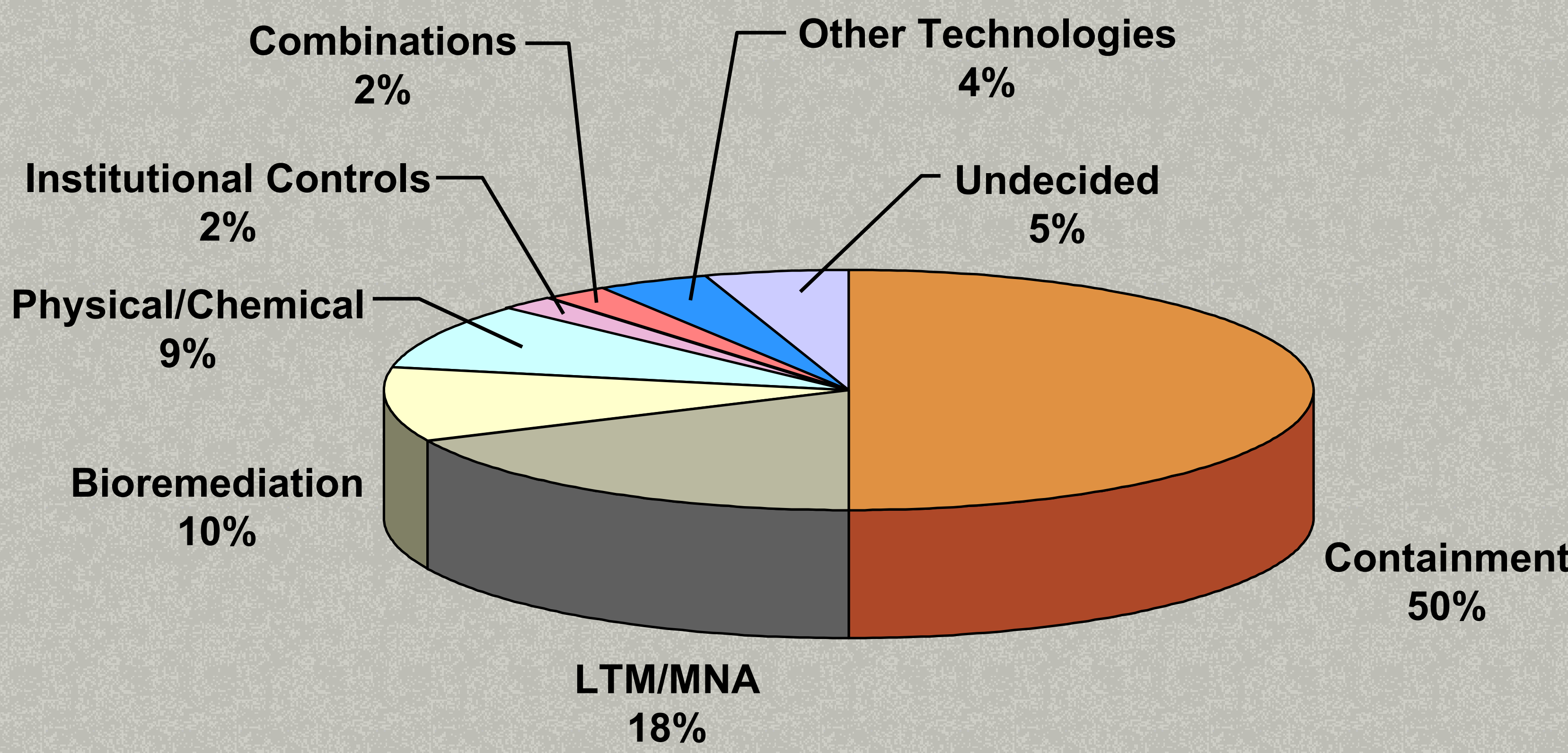
- Introduction: Science vs. Technology
- Plume Treatment
- NAPL Source Zone Treatment
- The DNAPL Problem
- Summary and Conclusions

DON's DNAPL Problem

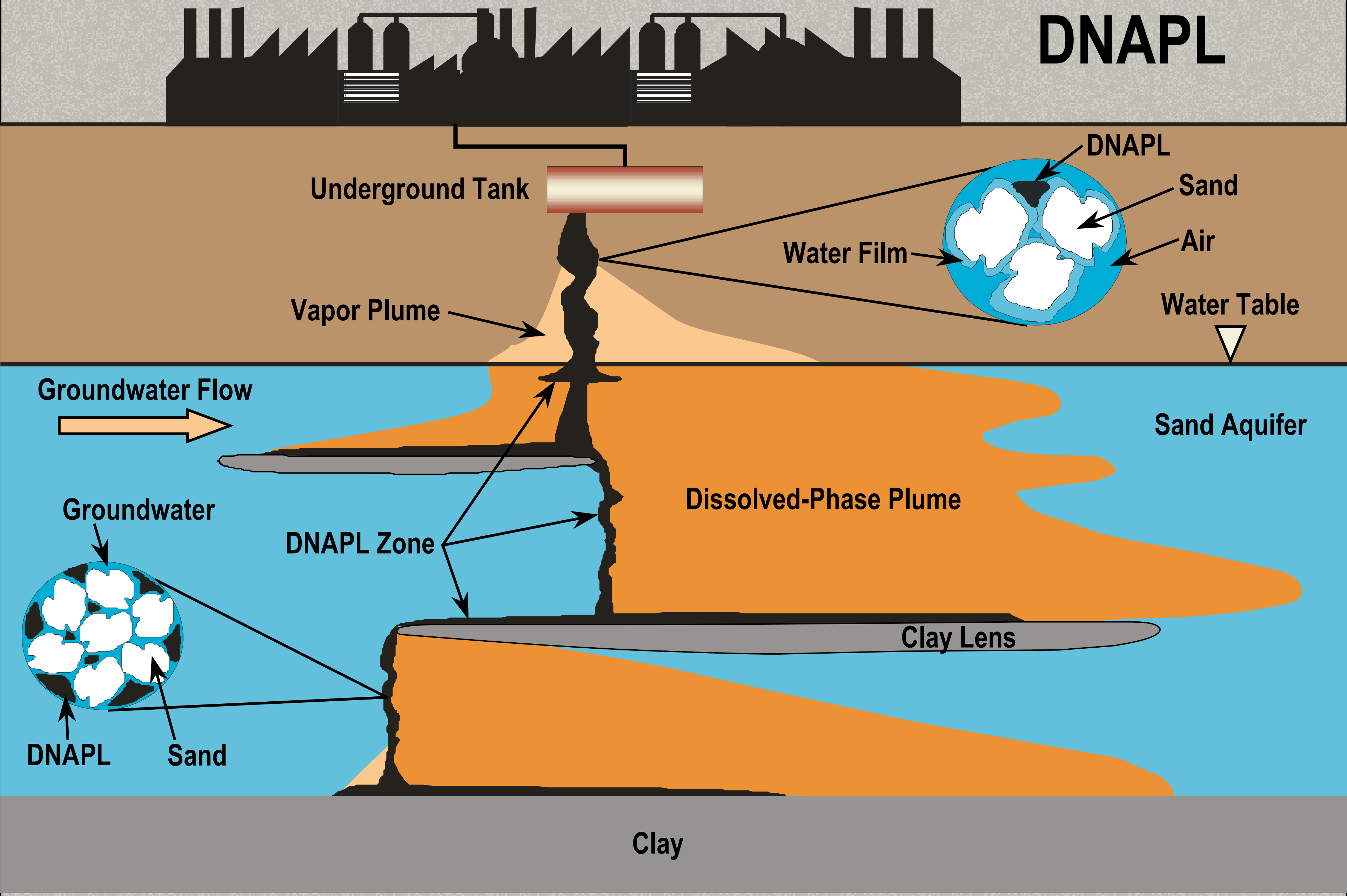
- 867 sites with chlorinated solvent contamination
- On 242 installations
- 50% are in the Remedial Action Phase
- Projected cost to complete is $1,830,000,000

Source: NORM Database, 2001

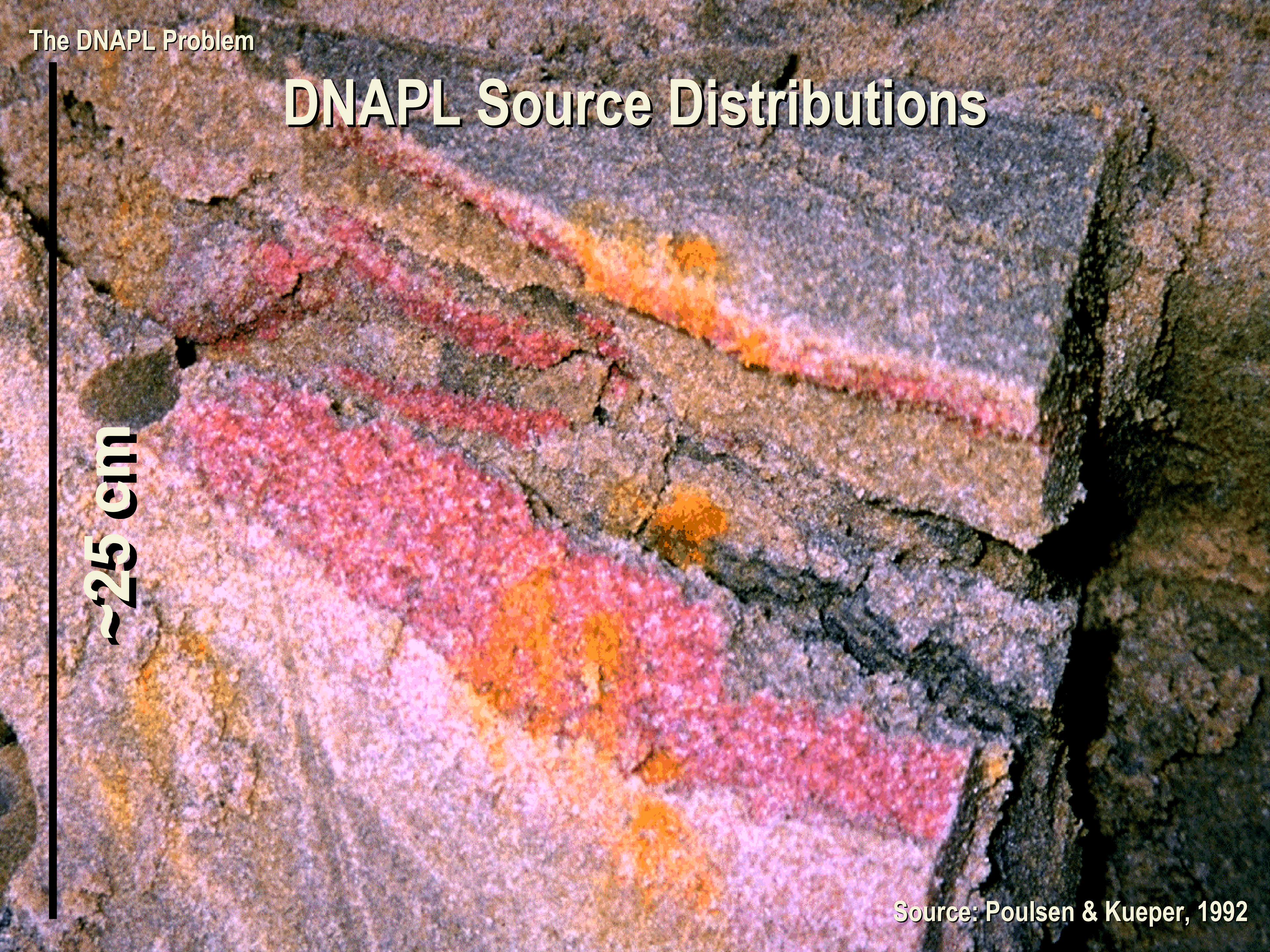
Remedies Proposed or In Use at DON Sites



The DNAPL Problem



DNAPL Source Distributions



Source: Poulsen & Kueper, 1992

The Matrix Diffusion Problem

- In any heterogeneous geology, chlorinated compounds will diffuse from more permeable zones (strata or fractures) into less permeable zones.
- The result is that no technology dependent on movement of some reactant or of the contaminant will be very effective in the treatment of this low-permeability material.
- Although all technologies depend to some extent on movement of reactants or contaminants, the thermal technologies are the less dependent upon this phenomenon.

The Characterization Problem

- Finding, delineating, and understanding source areas requires resolution on the order of a few feet.
- No known technology gives us that kind of resolution.
- DoD sites frequently have numerous small and diffuse sources. These are particularly hard to find and characterize.
- Source characterization vs. remediation cost is a cost/benefit issue. More characterization means more cost-effective remediation, but costs money itself.

Characterization Technologies

- Conventional soil and groundwater sampling is useful, but is rarely affordable in sufficient resolution.
- Conventional soil gas surveys can be a cost-effective way to locate release points and vadose contamination.
- Some emerging technologies are worth watching (i.e., membrane interface probes [MIPs]).
- Geophysics has been tried extensively with limited success.
- Partitioning Interwell Tracer Tests (PITTs) have utility but are expensive and have limitations.

DNAPL Source Treatment Technologies

There are technologies available that have been shown to remove DNAPL mass, and in some cases, to reduce groundwater concentrations in localized areas and/or for limited time.

- In Situ Thermal Treatment
- In Situ Oxidation
- In Situ Enhanced Flushing
- In Situ Bioremediation
- Miscellaneous others

When Will We Have Reliable Source Zone Technology?

What RPMs Need to Know

- No large DNAPL site has yet been cleaned up to MCLs
- A very few small sites probably have been.
- We've been trying 20 years.
- For the last 19 years, there has been an emerging technology that looked like it was promising.
- We are getting better.
- Many regulators and senior managers do not recognize this is true.

Rob's Top 10

- If you have a persistent dissolved chlorinated solvent plume, you probably have a source. Dissolved plumes without a source are mostly mythical.
- The chlorinated solvents may be in an LNAPL.
- The DNAPL release may have been sufficiently small that contamination does not penetrate deeply into the aquifer.
- The DoD has more plumes with small dispersed multiple sources than those conventionally published.
- You probably will never fully characterize your source(s).

Rob’s Top 10 (cont.)

- You will never be able to fully communicate to your management or to the public the problematic nature of DNAPL and LNAPL plumes.
- No large DNAPL sites have been remediated to MCLs, or even close; very few, if any, small sites have been.
- No technology exists or appears to be emerging that will substantially change number 4.
- There will always be a vendor with a technology that is "about to change" number 4.
- At many sites you will have to attempt source remediation anyway.

Summary

- Cleanup technology development is only two decades old.
- Explosion of technology/science effort in last 10 years.
- When intuitive approaches fail, we do the science to find out why, and solutions seem counterintuitive.
- If the science was completed first, then the technologies that follow would probably seem intuitive.
- Bottom Line: The “Bike” model is probably the only way we could have responded in 10-20 years, and the science is starting to catch up.

Moral of This Story

- In the cleanup business, technologies have rarely performed completely as expected and/or marketed.
- RPMs should understand the state of the **Science** and fully understand the performance and technical limitations associated with a **Technology** before buying.
- **Buyer-Beware: Don't "Take a Header" twice.**
- Somehow, the RPM needs to understand these issues, make the best decisions possible, and effectively communicate the issues to upper management, regulators, and the public. It's a cruel world out there….

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